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METHYL SALICYLATE I.—THE SEPARATION OF SALICYLIC ACID FROM METHYL SALICYLATE AND THE HYDROLYSIS OF THE ESTER.

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(From the Chemical Laboratory, Bureau of Science, Manila, P. I.)

Since salicylic acid and the salicylates have been prohibited in foods,[1] it becomes necessary in many cases to separate salicylic acid and its metal salts from its esters.

The methyl ester, either the synthetic preparation or oil of gaultheria, or oil of betula, is often found to be a constituent of many non-alcoholic beverages, such as the so-called root beers, sarsaparillas, and soda-water flavors. The United States Pharmacopœia and the National Formulary [2] authorize its use as a flavoring agent, and it is therefore often found in emulsions, the most common of which is cod-liver oil and other pharmacopœial preparations.

Salicylic acid or its salts and its methyl ester may be, and often are, found together in the above preparations; *first,* through the incorporation of both in the original mixture; *second,* when methyl salicylate, or oil of gaultheria, alone is used the ester may contain varying amounts of free salicylic acid as an impurity; *third,* when a comparatively pure ester is employed, free salicylic acid may subsequently become a constituent of the compound through the hydrolysis of the ester.

Regarding the first of these sources, it is sufficient to note that preservatives of various kinds, borax and boric acid, benzoic and salicylic

[1] *U. S. Dept. Agric., Food Inspection Decision* 76 (1907).

[2] 3d ed. (1906), 46.

acids, have been found by the writer and other investigators in soda-water flavors, root beers, sarsaparillas and cod-liver oil emulsions, both when methyl salicylate was present and absent, and several manufacturers have verified the findings by submitting their formulas for some of these preparations. In many cases it is possible that a preservative, in addition to the methyl salicylate, is quite superfluous, the ester probably having antiseptic qualities [3] sufficient to render the employment of other sterilizing agents or processes unnecessary.

Concerning the second source of salicylic acid, namely, as an impurity in the methyl salicylate, an examination of all of the different samples available in this laboratory and in the city of Manila, eight in all, has revealed the presence of the free acid in every case. Two of these samples were represented to be genuine oil of gaultheria, and six were synthetic preparations. All were of European exportation and had been in stock in this city from a few days to over a year. The amounts of free salicylic acid varied from a trace in one laboratory sample to 0.025 per cent by weight in a genuine oil of wintergreen. These small amounts do not wholly account for the larger quantities of salicylic acid or its salts which have been found in a number of different preparations upon the local markets and entering the port of Manila.

The third source, namely, the hydrolysis of the ester, will be shown [4] to account, in many cases, for the presence of free salicylic acid in preparations in which comparatively pure methyl salicylate has been employed as an ingredient. With alkalies the rate of hydrolysis is very rapid; it is slower with acids, and even with distilled water the hydrolysis is measurable. The temperature is an important factor of the rate. It is therefore not surprising that the formation of salicylic acid from methyl salicylate in this way is quite appreciable in foods or drugs which have been shipped by vessels to this port. The temperature of the holds of the vessels often rises above 30° in the tropics. The voyage by fastest steamers from Europe or the United States occupies about one month and by sailing vessels a number of months, and during the entire voyage the rolling and pitching of the vessel produces a constant agitation of the contents of bottles, casks and other containers, maintaining, in all, favorable conditions for hydrolysis.

THE DETERMINATION OF SALICYLIC ACID IN METHYL SALICYLATE.

The free acid can be titrated directly. The indicators which have been found to be applicable are Congo red and erythrosin. Alfred J. Cohn [5] says, "Congo red may be used for estimating mineral acids in the

[3] It is hoped that this investigation will form a part of a later paper.

[4] While this phase of the question will be touched upon here, it will be further dealt with in a later paper.

[5] Indicators and Test Papers, J. Wiley & Sons, New York (1904), 56.

presence of organic acids, as the latter do not affect it." This has been found to be an error, as salicylic acid can be accurately titrated, the end point being very sharp when either standard sodium hydroxide, carbonate or bicarbonate solutions are used, the carboxyl group only being affected. Walker and Wood [6] have used Congo red for titrating salicylic acid against baryta. Erythrosin has also been found to give fairly good results, although Congo red has been used almost entirely throughout this work.

In titrating the free acid in methyl salicylate, from 5 to 20 cubic centimeters of the ester are shaken with an equal quantity of neutral, distilled water in a glass-stoppered flask, and standard alkali, $\frac{N}{50}$, added until the color indicating the end point remains permanent on shaking.

Standard solutions of sodium acid carbonate[7] are best used in this titration, for reasons explained further on, although sodium hydroxide solutions give accurate results. The titrations were carried out at the room temperature, which varied in this laboratory from 28° to 34°.

In order to show that the acidity of the samples was not due to acids other than salicylic, the following method was employed: Ten cubic centimeters of the ester or oil of gaultheria were extracted three times with 5 cubic centimeter portions of $\frac{N}{10}$ sodium acid carbonate. The acid carbonate solutions were united, extracted three times with chloroform to remove the ester which was in solution, made acid with sulphuric acid (1 to 3) and extracted three times with chloroform. The chloroform extracts were united, filtered into a weighed dish, and evaporated spontaneously in a vacuum desiccator. After weighing the residue, it was dissolved in hot water and the salicylic acid determined colorimetrically.[8]

TABLE I.—*Amounts of salicylic acid in natural and artificial oil of gaultheria.*

Sample.	Amount.	Salicylic acid—		
		By titrating.	By weighing.[9]	Colorimetrically.
	cc.	*Per cent.*		*Per cent.*
Oil of gaultheria (genuine)	10	0.025	5.5 mg. = 0.046 per cent	0.028
Synthetic	10	0.0113	3.9 mg. = 0.033 per cent	0.0113

[6] *J. Chem. Soc.* (1898), **73**, 619.

[7] Standard solutions were made from Kahlbam's sodium acid carbonate, which was found to be very pure.

[8] Methods of Analysis, *Bull. U. S. Dept. Agric.* (1907), **107**, 180.

[9] The weights of the salicylic acid are evidently too great for the reason that drying was imperfect. Small quantities of the acid are so easily volatilized that it was considered preferable to err in the opposite direction and rely upon the colorimetric method for accuracy.

SEPARATION AND DETERMINATION OF SALICYLIC ACID AND METHYL SALICYLATE IN FOODS AND DRUGS.

The substance under investigation, containing salicylic acid and methyl salicylate, is made strongly alkaline to Congo red with an approximately normal solution of pure sodium acid carbonate, free from normal carbonate[10] and, if not homogeneous, the aqueous solution is separated and the process repeated with the residue until it is thoroughly extracted by the sodium acid carbonate solution. All of the salicylic acid has now passed into the acid carbonate solution in the form of sodium salicylate together with small amounts of methyl salicylate. This solution is extracted repeatedly, not less than three times, with small amounts of chloroform[11] until all traces of methyl salicylate have been removed. The sodium acid carbonate solution is now made acid with sulphuric acid (1 to 3) and extracted in the usual way to remove and determine the salicylic acid.[12]

This method has been successfully applied to emulsions of cod-liver oil which are usually very difficult to separate. The sodium acid carbonate layer, carrying the salicylic acid and small amounts of methyl salicylate, can be separated in a rapidly revolving centrifuge. With non-alcoholic beverages and soda-water flavors, the method is especially easy of manipulation. During the process of extraction, while the methyl salicylate is still in the solution with the salicylic acid salts, the temperature should not be unduly raised for the reason that the rate of hydrolysis of methyl salicylate is accelerated with increase in temperature. During the manipulation in this laboratory, where the temperature is always high, the solutions have been kept below 35°, which temperature has been found to be a fairly safe limit. Lower working temperatures are, of course, to be desired.

The ester, separated by chloroform extraction,[13] is saponified by heat-

[10] Solutions of sodium acid carbonate lose carbon dioxide and therefore should be freshly prepared and kept in well-stoppered bottles. The loss of carbon dioxide, the increase of normal sodium carbonate, and consequent increase of sodium hydroxide in the solution is in most cases counterbalanced by the acidity of the substance under examination. When this substance is very acid it is best made alkaline by the addition of solid sodium acid carbonate in order to avoid a great increase in the bulk of the solution.

[11] Chloroform has been found to be better than ether for removing the methyl salicylate from this solution, for the reason that it is less miscible with the aqueous solution.

[12] Methods of Analysis, *Loc. cit.*

[13] In the case of oil emulsions and some other mixtures the ester is best separated, after the removal of the salicylic acid, by steam distillation from a sulphuric-acid solution. Since methyl salicylate is partially hydrolyzed on heating in a sulphuric-acid solution, it is necessary to carry on the distillation until all of the salicylic acid formed has passed over into the receiver.

ing in a flask with reflux condenser attached, on a steam bath, with a large excess of strong caustic alkali solution.

After saponification is complete, half an hour usually being sufficient, the condenser is detached and the heating is continued until all of the chloroform is expelled. The solution is then diluted to a known volume and the salicylic acid determined in aliquot portions. The following quantitative experiments serve to show the manipulation and the accuracy of the method.

1.0256 grams methyl salicylate were dissolved in 50 cubic centimeters of chloroform and 10 cubic centimeter portions saponified with 10 cubic centimeters of a 25 per cent solution of caustic potash. After evaporation of the chloroform, the residue was diluted to 100 cubic centimeters and 2 cubic centimeter portions made acid with sulphuric acid (1 to 3) and extracted four times with small amounts of chloroform. The chloroform was evaporated in a vacuum desiccator, and the residue dissolved in 100 cubic centimeters hot water. The salicylic acid determined colorimetrically[14] in this solution gave 1.0640 grams methyl salicylate.

1.2277 grams treated as above gave 1.2667 grams.

0.1568 grams dissolved in 10 cubic centimeters of a 25 per cent solution of sodium hydroxide gave—

I.	II.
0.1499 gram.	0.1565 gram.

THE HYDROLYSIS OF METHYL SALICYLATE WITH SODIUM CARBONATE AND SODIUM HYDROXIDE.[15]

Solutions of sodium hydroxide, approximately $\frac{N}{5}$ and $\frac{N}{10}$, were made by dissolving clean, metallic sodium in distilled water from which the gases had been expelled by boiling. These were agitated in bottles with an excess of methyl salicylate and 10 cubic centimeter portions were removed and titrated at intervals.[16] The reactions were all carried on at 30°, with variations not exceeding $\pm 1°$. This is the prevailing temperature in this locality.

In the following tables, t is the time expressed in hours, v the volume of $\frac{N}{10}$ sulphuric acid used to neutralize 10 cubic centimeters of the reaction solution at time t, and x is the percentage of sodium hydroxide which has been used in the reaction.

[14] Color comparisons made with a wedge colorimeter.

[15] More extended investigation of the hydrolysis of methyl salicylate with acids, alkalies and water and the catalytic action of tropical sunlight is being carried on and will probably be presented in a later paper. The cases of sodium carbonate and hydroxide are here taken up merely to show the basis of the analytical methods.

[16] Ostwald-Luther: Physiko-Chemische Messungen, Leipzig (1902), 447.

TABLE II.—*Hydrolysis of methyl salicylate by sodium hydroxide.*

0.203 normal NaOH; T = 30° ± 0.5°.

t	v	x	t	v	x
0	20.30	0.00	6	2.30	88.67
1	14.70	27.58	7	1.70	91.62
2	9.60	52.70	8	1.25	93.84
3	6.65	67.24	24	0.30	98.51
4	4.60	77.34	31	0.20	99.01
5	3.30	83.74			

0.099 normal NaOH; T = 30° ± 0.5°.

11	0.30	96.96	18	0.15	98.48
15	.20	97.97	35	.10	99.00

$\frac{N}{5}$ sodium carbonate solutions were made from the pure salt and also from the carbonate formed by the ignition of sodium oxalate. A large excess of the ester was used in every case.

TABLE III.—*Hydrolysis of methyl salicylate with sodium carbonate.*

FIRST SERIES.

0.2 normal Na_2CO_3; T = 30° ± 1°.

t	v	x	t	v	x
0	20.0	0.0	32	14.20	29.0
1	19.4	3.0	48	13.2	34.0
2	19.1	4.5	56	12.9	35.5
3	18.7	6.5	72	12.35	38.25
5	18.1	9.5	80	12.1	39.5
7	17.65	11.75	125	11.46	42.7
8	17.3	13.5	144	11.28	43.6
24	14.9	25.5	152	11.24	43.8
28	14.4	28.0	168	11.2	44.0
31	14.25	28.75	194	11.1	44.5

SECOND SERIES.

8	17.5	12.5	64	12.65	36.75
9	17.1	14.5	80	12.15	39.25
10	17.0	15.0	88	11.97	40.15
11	16.8	16.0	133	11.40	43.0
13	16.5	17.5	152	11.2	44.0
14	16.2	19.0	160	11.22	43.9
16	15.9	20.5	176	11.18	44.1
32	14.25	28.75	202	11.02	44.9
33	14.1	29.5	225	11.0	45.0
36	13.9	30.5	254	10.95	45.25
39	13.75	31.25	323	10.7	46.5
40	13.7	31.50	489	10.45	47.75
56	12.9	35.5			

TABLE III.—*Hydrolysis of methyl salicylate with sodium carbonate*—Continued.

THIRD SERIES.

16	15.8	21.0	96	11.9	40.5
17	15.65	21.75	141	11.3	43.5
18	15.5	22.5	160	11.2	44.0
21	15.25	23.75	168	11.2	44.0
23	15.1	24.5	184	11.15	44.25
24	14.9	25.5	210	11.0	45.0
40	13.7	31.5	233	10.9	45.5
44	13.4	33.0	262	10.88	45.6
48	13.3	33.5	497	10.40	48.0
64	12.7	36.5	624	10.2	49.0
72	12.45	37.75	665	10.13	49.35
88	12.0	40.0	737	10.00	50.00

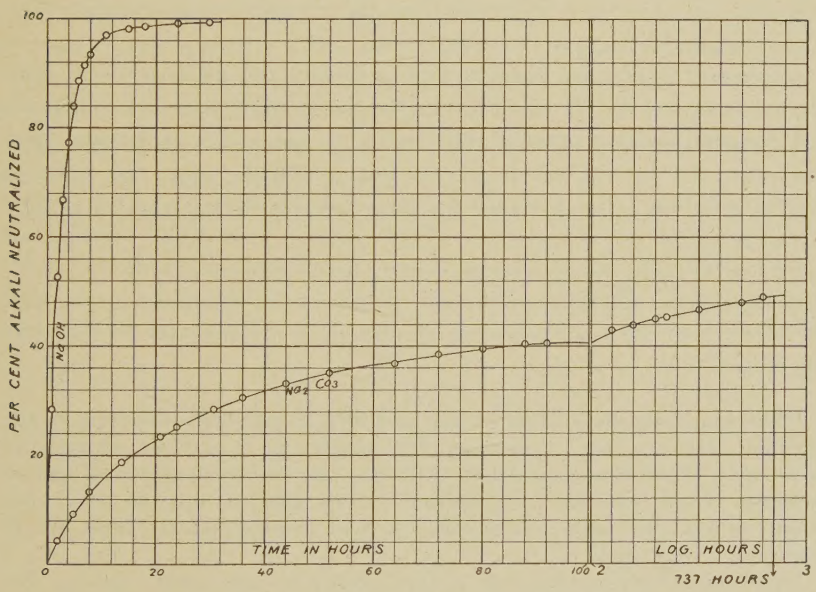

FIG. I.—HYDROLYSIS OF METHYL SALICYLATE.

The rate of hydrolysis with sodium carbonate is a smooth curve, the break in the diagram being due to the change of scale.

The curves shown in fig. 1 are constructed from the above tables. It is to be noted that the hydrolysis of the ester with sodium hydroxide goes to completion; that is, to the point where all of the hydroxide has been used in the reaction, or at least it goes very nearly to completion in about twenty-four hours. With sodium carbonate, equilibrium, for all practical purposes, is reached in about one month, at the point where all of the

normal carbonate has been converted into the acid carbonate according to the equation: [17]

$$C_6H_4 . OH . COOCH_3 + Na_2CO_3 = C_6H_4 . OH . COONa + CH_3OH + NaHCO_3$$

To prove that this is the end point of the reaction, or at least the point where the rate is exceedingly slow, the ester was shaken for days with pure $\frac{N}{10}$ sodium acid carbonate [18] solution in a number of sealed tubes. While a slight reaction was noted, it is believed that the substances were practically in equilibrium.[19] Any reaction taking place is not sufficiently rapid to affect the accuracy of the analytic methods previously described, which depend upon sodium acid carbonate for the removal of salicylic acid as sodium salicylate from the presence of the methyl ester, without saponification of the latter.

Cahours [20] says that concentrated solutions of alkalies react with methyl salicylate in the cold to produce the salts of the ester. Freer [21] has prepared sodium salicylic ethyl ester by the action of sodium upon the ester and by the action of sodium hydroxide upon the ester in etherial solution. He mentions the fact that the compound thus formed is easily hydrolized by moisture. The reactions with dilute solutions of sodium hydroxide and sodium carbonate, here described, are hydrolytic.[22] Analyses of the solutions at the end points of the reactions, prove that the products of the saponifications are present in the amounts indicated by the theory.

[17] The hydrolytic dissociation of sodium hydrogen carbonate according to the equation: $NaHCO_3 + H_2O \rightleftharpoons NaOH + H_2CO_3$ necessitates a gaseous pressure of carbon dioxide and a continuous loss of the gas with formation of normal sodium carbonate in the solution. A discussion of this question may be more fully entered into a later paper. It is sufficient here to note that the effect due to this cause is very slight.

[18] The amount of the hydroxide in this solution is very small. McCoy, *Am. Chem. J.* (1903), **29**, 453, has calculated the concentration to be 2.9×10^{-6}.

[19] A more detailed discussion will be taken up in a later paper.

[20] *Ann. Chim. Phys.* (1844) (3) **10**, 327.

[21] *Am. Chem. J.* (1892), **14**, 411.

[22] Secondary reactions take place, to a small extent, not sufficient to affect the accuracy of the method. Some of these, probably due to light rays, are being studied.

TABLE IV.—*The analyses of the solutions described in Tables II and III at the end of the reactions.*

Solution.	Methyl alcohol.		Salicylic acid.	
	Theoretical.	Found.	Theoretical.	Found.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
0.203 normal NaOH	0.64	0.67	2.80	2.66
0.099 normal NaOH	0.32	----------	1.37	1.41
0.2 normal Na_2CO_3	0.32	0.314	1.38	1.33

SUMMARY.

It is shown that methyl salicylate (synthetic), or oil of gaultheria, when used in foods and drugs, may give rise to the presence of salicylic acid, first, as an impurity in the ester; second, through its hydrolysis.

Methods for the separation and quantitative estimation of salicylic acid and methyl salicylate are described.

The rate of saponification of methyl salicylate in solutions of sodium hydroxide and carbonate are studied.

The work in some of its other phases is being continued.

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NOTES ON THE SPROUTING COCONUT, ON COPRA, AND ON COCONUT OIL.

By Herbert S. Walker.

(*From the Chemical Laboratory, Bureau of Science, Manila, P. I.*)

CONTENTS.

I. Experiments on Enzymes in the Coconut.
II. Changes in the Composition of the Coconut while Sprouting.
III. The Action on Copra of Microörganisms in Pure Culture.
IV. The Production of Free Acid in Commercial Coconut Oil on Long Standing.

I. EXPERIMENTS ON ENZYMES IN THE COCONUT.

The following experiments were made in an endeavor to discover if the coconut, like the castor bean and many other oil seeds, contains a fat-splitting enzyme capable of saponifying outside of the growing nut.

COCONUT FOOT.

Experiment I.—One hundred grams of the fresh foot in a sprouting coconut were ground with sand and water, and the expressed liquor was strained through cloth. One per cent of toluol was added and the whole allowed to stand on ice over night.

(*a*) Five cubic centimeters of water, 1 of *fresh liquor* and 0.25 of ethyl butyrate were kept in a water bath at 40° for fifteen minutes and then titrated; there were required 0.48 cubic centimeters of $\frac{N}{10}$ potassium hydroxide for neutralization. The mixture was allowed to stand until the next day, when it took 0.12 cubic centimeter more of the same solution of alkali.

(*b*) Five cubic centimeters of water, 1 of the *boiled liquor* and 0.25 of ethyl butyrate were placed under the same conditions as the above for fifteen minutes in a water bath; there were required for neutralization 0.45 cubic centimeters of $\frac{N}{10}$ potassium hydroxide and on the next day 0.11 cubic centimeter more.

(*c*) Five cubic centimeters of water, 1 of *fresh liquor*, 0.25 of ethyl butyrate, 1 drop of phenolphthaleïn, 0.28 cubic centimeter of $\frac{N}{10}$ potassium hydroxide and 0.1 of toluol were placed in a water bath for thirty minutes, then stood at room temperature until the next day, when 0.09 cubic centimeters of $\frac{N}{10}$ potassium hydroxide were required for neutralization.

(*d*) The conditions were the same as in (*c*) with the exception that boiled

liquor was used. There were required 0.12 cubic centimeter $\frac{N}{10}$ potassium hydroxide for neutralization.

Conclusion.—No enzyme capable of hydrolizing ethyl butyrate is present in the press liquor from the coconut foot.

For comparison I give one experiment by Kastle and Loevenhart[1] working with a 10 per cent extract obtained from the pancreas of a pig.

One cubic centimeter extract, 4 of water, 0.26 of ethyl butyrate and 0.1 of toluol were kept at 40° for fifteen minutes and showed an increase in acidity corresponding to 1.63 cubic centimeter $\frac{N}{10}$ potassium hydroxide. A similar test with the boiled extract showed no increase in acidity whatsoever.

My *Experiment I* was continued as follows:

(*e*) Eight cubic centimeters of *fresh liquor*, 5 of coconut oil and 0.1 of toluol were allowed to stand one week. Eight cubic centimeters of $\frac{N}{10}$ potassium hydroxide were required for neutralization.

(*f*) Eight cubic centimeters of *boiled liquor*, 5 of coconut oil, and 0.1 of toluol were allowed to stand one week. 19.9 cubic centimeters $\frac{N}{10}$ potassium hydroxide were required for neutralization.

The boiled liquor showed a considerably greater acidity on standing than did the fresh, hence it is evident that no hydrolysis by enzymes had thus far been proved. The nut from which this foot was taken was perfectly sound and free from mold, but the inner surface of the meat next to the foot had begun to soften and had a greasy feel. A portion of this softened meat was dried and expressed, yielding an oil containing 3.3 per cent of free fatty acids, showing that hydrolysis to a marked extent had taken place in the growing nut.

COCONUT MEAT.

Experiment II.—The sprouting nut used for this series contained a foot which almost filled it. The meat remaining was ground in a sausage grinder and a cream-like emulsion pressed out.

(*a*) *The action with ethyl butyrate.*—The conditions were; 5 cubic centimeters of water, 0.25 of ethyl butyrate, 1 of toluol and 1 of cream, with the following result:

Conditions.	1½ hours at 40° C.	Neutralized, let stand at room temperature 1 day.	Let stand 1 day more at room temperature.	Not neutralized, room temperature for 2 days.
Fresh cream	0.45 cc. $\frac{N}{10}$ KOH	0.12 cc. $\frac{N}{10}$ KOH	0.10 cc. $\frac{N}{10}$ KOH	0.92 cc. $\frac{N}{10}$ KOH
Boiled cream	0.35 cc. $\frac{N}{10}$ KOH	0.10 cc. $\frac{N}{10}$	0.10 cc. $\frac{N}{10}$ KOH	0.45 cc. $\frac{N}{10}$ KOH

[1] *Amer. Chem. Journ.* (1900) **24**, 491.

(*b*) The *cream alone* with 1 per cent of toluol as an antiseptic was allowed to stand four days in the incubator.

(1) Five cubic centimeters of boiled cream required 7 cubic centimeters of $\frac{N}{10}$ potassium hydroxide to neutralize.

(2) Five cubic centimeters of fresh cream required 12.8 cubic centimeters of $\frac{N}{10}$ potassium hydroxide to neutralize.

(*c*) After pressing out the cream used in (*a*) and (*b*), the residue was ground with sand and water and two fractions pressed out in the hydraulic press: A (up to 250 kilograms per square centimeter) and B 250 to 450 kilograms). These samples were kept under the same conditions as in (*b*) for four days and aliquot portions, each of 5 cubic centimeters, were titrated with $\frac{N}{10}$ potassium hydroxide. The following is the result:

A, boiled and fresh, and B, boiled and fresh, each took 0.05 cubic centimeter of $\frac{N}{10}$ potassium hydroxide to neutralize.

The cream from the first pressing (*a*) is therefore the only one showing any indication of enzyme activity.

(*d*) Five cubic centimeters of the cream from the first pressing (*a*), 5 of coconut oil and 2 of toluol were placed in an incubator for four days; there were required 12.4 cubic centimeters of $\frac{N}{10}$ potassium hydroxide for neutralization. A control made under the same conditions with boiled cream required 6.6 cubic centimeters.

The greater increase in acidity of the unboiled cream seemed at first to indicate enzyme action; but plate cultures made from the two tubes showed a considerable number of mold and bacterial colonies, these being more numerous in the unboiled than in the boiled cream. Therefore, it seems more reasonable to attribute the increase in acidity to the inefficiency of the antiseptic used, rather than to a specific enzyme action.

COCONUT MILK.

Experiment III.—The nut used had begun to sprout, its inner space being almost completely filled by the endosperm. About 50 cubic centimeters of milk were obtained and tested, the conditions being as follows: 5 cubic centimeters of water, 0.25 of ethyl butyrate, 1 of toluol and 1 of milk.

Conditions.	15 minutes at 40°.	12 hours at 35–40°.
Unboiled	0.28 cc. $\frac{N}{10}$ KOH	0.35 cc. $\frac{N}{10}$ KOH
Boiled	0.28 cc. $\frac{N}{10}$ KOH	0.38 cc. $\frac{N}{10}$ KOH

The results show no evidence of the presence of an enzyme in coconut milk.

MEAT AND MILK.

Experiment IV.—(*a*) The expressed cream from the meat of a nut just beginning to sprout was used, the conditions being as follows:

Five cubic centimeters of water, 0.25 of ethyl butyrate, 1 of toluol and 1 of cream.

Conditions.	At start.	Neutralized, and let stand 24 hours.	Not neutralized.		
			Room temperature 24 hours.	Incubator 24 hours.	
				a.	b.
		cc.	*cc.*	*cc.*	*cc.*
Unboiled	0.47 cc. $\frac{N}{10}$ KOH	0.18	1.82	1.24	2.00
Boiled	0.47 cc.	0.16	0.70	0.60	0.47

(*b*) Five cubic centimeters of water, 0.25 of ethyl butyrate, 1 of 1 to 1,000 formalin and 1 of cream were used. The unboiled mixture after twenty-four hours at room temperature took 0.55 cubic centimeter of $\frac{N}{10}$ potassium hydroxide and the boiled mixture 0.48 to neutralize.

Here again, although the unboiled cream increases in acidity fairly rapidly in the presence of toluol, the increase must be due chiefly to inefficient antisepsis, as it is almost entirely inhibited by formalin in a dilution of 1 to 7,000. Experiment has shown that formalin of this strength has practically no action on enzymes.

Experiment V.—The cream used in *Experiment IV* was treated with alcohol and ether, the precipitate washed with alcohol and finally with ether and then dried in a vacuum over sulphuric acid. One gram of this powder rubbed up with 20 cubic centimeters of water yielded a milky liquor which was tested for the presence of enzymes, the following being used:

Five cubic centimeters of water, 0.25 of ethyl butyrate, 1 of toluol and 1 of the liquor, the mixture being kept in the incubator at 35° to 40° for two days.

Both the boiled and unboiled liquor required 0.8 cubic centimeter of $\frac{N}{10}$ potassium hydroxide to neutralize.

It is evident that the precipitate obtained from coconut cream by the above method contains no fat-splitting enzymes.

COCONUT FOOT AND COCONUT OIL.

Experiment VI.—(*a*) One hundred grams of foot from two nuts with sprouts about 1 meter long were mixed in a mortar with 100 cubic centimeters of fresh coconut oil, 100 of water and 1 of chloral. The mixture was well ground for about one hour to prepare a good emulsion, it was then strained through cloth and 25 cubic centimeter portions were placed in small, stoppered Erlenmeyer

flasks. The samples were then titrated at various intervals with $\frac{N}{10}$ potassium hydroxide, the result being given in cubic centimeters required to neutralize:

Time.	Cubic centimeters.
At once	13.5
1 day	12.0
2 days	12.2
7 days	13.8
8 days	18.5

Cultures made at the end of the last period showed the presence of molds and bacteria.

(*b*) One hundred grams of meat from the same nuts as were used in (*a*) were ground with 75 cubic centimeters of fresh coconut oil, 75 of water and 1 of chloral; 25 cubic centimeters of the strained emulsion required the following amounts of $\frac{N}{10}$ potassium hydroxide for neutralization:

Time.	Cubic centimeters.
At once	10.0
1 day	11.0
2 days	11.5
7 days	24.0
8 days	27.5

Cultures made at the end of eight days showed that the flasks were no longer sterile; they had all become slightly discolored at this time and in some cases possessed a bad odor. The slight increase in acidity in this comparatively long term must therefore be attributed to the actions of organisms, not to enzymes.

ATTEMPTS TO RENDER AN ENZYME ACTIVE.

Connstein, Hoyer and Wartenberg,[2] working with lipase from the castor bean, have shown that its rapidity of action is greatly increased by the addition of a small amount of acid. The following experiments were made to discover if this might not likewise render active any enzyme of the coconut which might be present.

COCONUT FOOT AND COCONUT OIL WITH HYDROCHLORIC ACID.

Experiment VII.—(*a*) Fifty grams of the foot from a nut with sprout about 1 meter long were shaved into fine pieces and ground in a mortar, first with 2 grams of chloral hydrate, then with 50 grams of fresh coconut oil and finally with 25 cubic centimeters of $\frac{N}{10}$ hydrochloric acid. Ten cubic centimeter portions of

[2] *Ber. d. Chem. Ges.* (1902), **35**, 3988.

the resulting mixture were then placed in small, stoppered Erlenmeyer flasks and titrated from time to time with $\frac{N}{10}$ potassium hydroxide.

Time.	Cubic centimeters.
At once	10.0
1 day	10.0
3 days	11.5
5 days	10.5
8 days	11.0
14 days	11.3
23 days	11.0

The result shows that practically no hydrolysis had taken place in twenty-three days. The flasks at the end of this time remained sterile.

COCONUT MEAT WITH HYDROCHLORIC ACID.

(*b*) One hundred grams of meat from a nut with a sprout about 75 centimeters long were thoroughly ground with 2 grams of chloral hydrate and 50 cubic centimeters of $\frac{N}{10}$ hydrochloric acid; 10-gram samples of the mixture were placed in small, stoppered Erlenmeyer flasks and titrated with $\frac{N}{10}$ potassium hydroxide after the addition of absolute alcohol and phenolphthaleïn. The result was as follows:

Time.	Cubic centimeters.
At once	8.5
2 days	10.0
4 days	9.1
13 days	11.1
19 days	11.2
22 days	11.5

The flasks were practically sterile at the end of twenty-two days. The slight apparent increase in acidity may almost be accounted for by experimental error, as in a non-homogeneous mixture such as this an exact titration is exceedingly difficult.

EXPRESSED LIQUOR FROM FOOT AND MEAT OF A SPROUTING NUT IN EMULSION WITH COCONUT OIL AND GUM ACACIA.

Experiment VIII.—One hundred grams of foot from a sprouting nut, 100 of meat from the same nut, 100 of sand and 100 cubic centimeters of a 2 per cent chloral hydrate solution were ground together in a mortar for two hours and the whole mass expressed; there resulted a muddy liquor consisting of water and partially emulsified oil. Fifty grams of coconut oil were rubbed up with 20 grams of gum acacia and 100 grams of this press liquor to form a permanent emulsion, 10 cubic centimeter samples of which were transferred to flasks and

titrated with $\frac{N}{10}$ potassium hydroxide as in the previous experiments. The result was as follows:

Conditions.	At once.	2 days.	6 days.
	cc.	*cc.*	*cc.*
Press liquor+oil	7.0	6.7	9.2
Press liquor alone	9.7	9.5	12.3

No cultures were made from these flasks.

CREAM EXPRESSED FROM COCONUT MEAT, WITH ACETIC ACID.

Experiment IX.—(*a*) The entire meat from a nut with a sprout about 30 centimeters long was ground in a meat grinder and pressed in a hydraulic press up to 450 atmospheres, 50 cubic centimeters of the thick, cream-like press liquor, 25 cubic centimeters of a 1 per cent chloral hydrate and 2 per cent acetic acid solution were ground to an emulsion, weighed in separate portions of 10 grams each and titrated in alcoholic solution with $\frac{N}{10}$ potassium hydroxide.

Time.	Cubic centimeters.
At once	1.7
1 day	1.7
3 days	1.9
6 days	2.05
31 days	2.15

PRESS CAKE FROM MEAT, WITH COCONUT OIL AND ACETIC ACID.

(*b*) The press cake from (*a*) was dried over sulphuric acid at room temperature and ground to a fine powder; 2.5 grams of this powder with 22.7 of coconut oil and 10 of acid chloral solution were ground together for two hours in a mortar; 10-gram samples were taken for titration with $\frac{N}{10}$ potassium hydroxide with the following results:

Time.	Cubic centimeters.
At once	1.10
2 days	1.08
7 days	1.08

(*c*) A parallel experiment with the dried press cake from castor beans was made at the same time; 2.5 grams of the cake, 22.7 of coconut oil and 10 of acid chloral solution being ground together, and 10-gram portions were titrated with $\frac{N}{10}$ potassium hydroxide, with the result recorded below:

Time.	Cubic centimeters.
At once	2.7
1 day	12.4
2 days	15.0

EXTRACTED, DRIED AND PULVERIZED MEAT WITH COCONUT OIL AND ACETIC ACID.

Experiment X.—(*a*) The meat from a nut with a sprout about 30 centimeters long was cut into fine pieces and extracted with cold ether until practically all the oil was removed; the remainder was then dried in a current of air at room temperature, and finally in a vacuum over fused calcium chloride. When dry, it was ground to a fine powder and again dried over calcium chloride; 2.5 grams of this powder, 22.7 of oil and 10 of an acid chloral solution were ground together and 10-gram portions titrated with $\frac{N}{10}$ potassium hydroxide, with the following result:

Time.	Cubic centimeters.
At once	1.18
2 days	1.15
7 days	1.05

(*b*) The foot from same nut was extracted with cold ether, dried in a vacuum, and ground to a fine powder; 2.5 grams of this powder, 22.7 of oil and 10 cubic centimeters of acid-chloral solution were ground together and 10-gram portions used for titration with $\frac{N}{10}$ potassium hydroxide. There was practically no change, as is shown below:

Time.	Cubic centimeters.
At once	1.38
2 days	1.35
7 days	1.32

SUMMARY.

Experiments were first made with coconut meat, milk and the foot under varying conditions, to determine if they were capable of hydrolizing ethyl butyrate according to the methods employed by Kastle and Loevenhart, toluol being used as an antiseptic. In most cases no increase in acidity was noted. However, when hydrolysis did occur the tubes were found not to be sterile, the conclusion being that toluol is not a sufficiently strong antiseptic to prevent the growth of organisms in coconut extracts.

When formalin was used in a dilution of 1 to 7,000 the hydrolysis was entirely stopped. Formalin of this strength has almost no effect on enzyme action.

After this failure to hydrolize ethyl butyrate by means of extracts from the meat, milk and foot, attempts were made to emulsify and hydrolize pure coconut oil according to the method of Constein, Hoyer and Wartenberg, using different portions of the coconut, instead of castor beans. In no case were these attempts successful under sterile conditions, although parallel experiments carried on with castor bean press cake showed a decided hydrolysis.

In none of these experiments, which extended over a period of seven months, is the slightest proof given of the existence in the coconut of an enzyme capable of hydrolizing fat outside of the growing nut. The

cause for the destruction of the fat in the growing nut must therefore be sought elsewhere. A discussion of the changes taking place in the sprouting nut is given in the following chapter.

II. CHANGES IN THE COMPOSITION OF THE COCONUT WHILE SPROUTING.

Four pairs of sprouting coconuts of different ages but approximately of the same size were selected for this work and their composition determined as follows.

TOTAL WEIGHTS.

After measuring the length of the sprout, the total weights of the whole nuts (including the shell but free from husk), the milk, foot, meat and sprout (with roots) were determined at once.

MEAT.

Three samples of 10 grams each were taken from each nut for analysis, viz:

Ten grams from that portion of the meat nearest the foot;

Ten grams from that portion of the meat farthest from the foot;

Ten grams as an average sample of the remainder which in Table I is calculated on the total.

Moisture.—The materials were dried for five hours at 100° C.

Oil.—The dried meat was ground to a fine pulp in a mortar and extracted in a Soxhlet cone with chloroform.

Sugar.—After removal of the oil the remainder was extracted with 50 cubic centimeters of water for three hours in the same apparatus as was used for oil extraction, the solution was then placed in a 100 cubic centimeter flask, clarified with basic lead acetate, the excess of lead removed with potassium oxalate, the whole diluted with water to 100 cubic centimeters, filtered, and after inversion, the sugar determined in 25 cubic centimeters of the filtrate by Fehling's gravimetric method.

Crude fiber.—This was determined in the residue from the extraction with water, according to the method of the *Association of Official Agricultural Chemists.*

FOOT.

Sugar.—Ten-gram samples were ground to a fine pulp and placed in a 100 cubic centimeter flask with about 50 cubic centimeters of water, they were then allowed to stand at room temperature with occasional shaking for three or four hours and diluted to the mark after the addition of basic lead acetate and potassium oxalate. Twenty-five cubic centimeters of the filtrate were inverted and the sugar determined by Fehling's gravimetric method.

Crude fiber.—Determined according to method of the *Association of Official Agricultural Chemists.*

MILK.

Sugar.—Fifty-gram samples were clarified, diluted to 100 cubic centimeters and 10 cubic centimeters taken for the Fehling determination (equivalent to 5-gram samples).

FREE FATTY ACID IN THE OIL FROM THE MEAT.

After determining the percentage of oil in the meat, the oil was titrated in alcoholic solution with $\frac{N}{10}$ potassium hydroxide, phenolphthaleïn being used as an indicator.

The results are given in the following table:

TABLE I.—*Changes taking place in the coconut during sprouting.*

Number.	1.		2.		3.		4.		5.		6.		7.		8.	
Length of sprout in centimeters	Not sprouted 0		Not sprouted 0		4		9		38		39		93		93	
Total weight in grams of nut free from husk (including sprout, roots and shell)	1038		1004		895		860		855		1002		875		760	
Total weight in grams of milk	374		307		275		200		177		100		0		0	
Total weight in grams of foot	19		29		42		49		90		178		228		213	
Total weight in grams of meat	457		421		382		403		327		400		152		148	
Weight of sprout and roots	0		0		Not weighed.		Not weighed.		42		70		244		139	
	Weight.	Per cent.	Weight.	Per cent.	Weight.	Per cent.	Weight.	Per cent.	Weight.	Per cent.	Weight.	Per cent.	Weight.	Per cent.	Weight.	Per cent.
Oil in meat: 10 grams near foot	3.20	32.0	4.19	41.9	4.37	43.7	3.66	36.6	3.98	39.8	4.79	47.9	No meat near foot.			
Oil in meat: 10 grams opposite foot	3.16	31 6	2.96	29.6	2.71	27.1	2.62	26.2	3.17	31.7	3.69	36.9	3.42	34.2	5.57	55.7
Oil in meat: Balance	157.	35.9	135.	33.7	116.	32.2	121.	31.7	115.	37.3	165	43.5	49.4	37.4	72.	56.4
Water in meat: 10 grams near foot	5.40	54.0	4.24	42.4	4.18	41.8	4.92	49.2	4.53	45.3	3.70	37.0	No meat near foot.			
Water in meat: 10 grams opposite foot	5.27	52.7	5.25	52.5	5.73	57.3	5.88	58.8	5.24	52.4	4.65	46.5	5.12	51.2	2.62	26.2
Water in meat: Balance	175.	48.8	195.	48.7	190.	52.5	202.	52.8	161	47.5	157	41.2	63.1	47.8	33.5	26.5
Sugar in meat: 10 grams near foot	0.20	2.0	0.13	1.3	0.08	0.8	0.15	1.5	0.05	0.5	0.08	0.8	No meat near foot.			
Sugar in meat: 10 grams opposite foot	0.34	3.4	Determination lost.		0.43	4.3	0.42	4.2	0.36	3.6	0.36	3.6	0.15	1.5	0.08	0.8
Sugar in meat: Balance	18.0	4.1	14.8	3.7	10.6	2.9	14.4	3.8	7.9	2.6	6.5	1.7	2.0	1.5	1.05	1.2
Crude fiber in meat: 10 grams near foot	0.22	2.2	0.31	3.1	0.17	1.7	0.19	1.9	0.25	2.5	0.24	2.4	No meat near foot.			
Crude fiber in meat: 10 grams opposite foot	0.21	2.1	0.26	2.6	0.17	1.7	0.16	1.6	0.17	1.7	0.17	1.7	0.17	1.7	0.19	1.9
Crude fiber in meat: Balance	11.1	2.5	10.2	2.6	6.5	1.8	7.7	2.0	5.8	1.9	7.1	1.9	2.5	1.9	2.9	2.2
Crude fiber in foot	0.2	1.1	0.3	0.9	0.3	0.7	0.3	0.6	Determination lost.				6.1	2.7	3.8	1.8
Sugar in foot	1.7	8.1	2.6	9.1	2.7	6.4	3.1	6.4	4.0	4.8	9.1	5.1	22.1	9.7	27.7	13.0

DISCUSSION OF THE CHANGES TAKING PLACE.

Milk.—The total quantity of milk shows a marked diminution from 374 grams in an unsprouted nut to nothing when the sprouts have attained a height of 93 centimeters. A decided loss in the sugar content of the milk takes place at the same time, as this constituent falls from 2 per cent and 2.3 per cent in the milk from the unsprouted nuts to 0.3 per cent in the ones which have sprouts 38 centimeters in height.

Meat.—Here also a decided loss in total weight is evident, as it drops from 457 grams in nut number 1 to 148 grams in number 8. The loss seems to be due to a direct absorption by the foot, the process taking place at first only in that portion of the meat located near the *latter,* but increasing rapidly as the endosperm grows larger and comes in contact with the entire inner surface of the nut.

Oil in the meat.—The loss in total weight of oil is fairly proportional to the loss in total weight of meat, the percentage of oil in the meat remaining constant within the somewhat wide limits of individual variation. However, during the early stages of germination there is apparent a certain concentration of oil near the foot, with a corresponding loss in that portion of the meat farthest away.

Water in the meat.—As is the case with all the other parts of the nut, the meat gradually loses water by evaporation through the shell and sprout during the process of germination.

Sugar in the meat.—The percentage of sugar decreases from 4.1 per cent in the unsprouted nut (number 1) to 1.2 per cent in number 8. The loss is probably due to the absorption of sugar by the foot, as in all cases there is considerably less sugar in that portion of the nut in direct contact with the endosperm than there is in the parts farthest away from it.

Crude fiber in the meat.—No decided change in the proportion of this constituent can be observed. It is absorbed at practically the same rate as the rest of the meat.

FOOT.

Total weight.—The total weight increases from 19 grams in number 1 to 228 grams in number 7.

Sugar in the foot.—There is apparently a loss in the percentage of sugar (although not in its total weight) until the foot completely fills the nut, at which time there is a rapid gain. This phenomenon is probably due to the fact that the foot at first draws its sugar chiefly from the milk by which it is almost entirely surrounded. However, as it continues to grow, it soon exhausts the sugar in the milk, and only when it has completely filled the nut and come into intimate contact with the inner surface of the meat has it an opportunity to continue the process of sugar absorption and also one of sugar *creation,* possibly from the oil, or possibly from oil and crude fiber.

Crude fiber in the foot.—A slight increase in this constituent (from 1.1 per cent and 0.9 per cent in numbers 1 and 2, to 2 per cent and 1.8 per cent in numbers 7 and 8 respectively) will be noted.

If we consider the total weights of the constituents, oil, sugar, and fiber, the following changes may be remarked:

Oil.—A decrease from 163 grams in number 1 to 78 grams in number 8 is observed, or a total loss of 85 grams.

Sugar.—There appears to be a considerable loss in total weight of sugar during the intermediate period of germination, which is however again made up at the time the foot fills the entire nut. Increase in sugar takes place in the foot. Considering the first and last of the series, numbers 1 and 8, the following changes in sugar content have taken place:

Portion of the nut.	Loss.	Gain.
	Grams.	*Grams.*
Meat	17.0	
Milk	7.5	
Foot		26.0
Total	24.5	26.0

Crude fiber.—There is a slight loss in the total weight of fiber in foot and meat, which is more than made up by the increased weight of sprout and roots.

Free fatty acids and oil from the meat.—From the beginning, the oil from the meat nearest the foot is invariably richest in fatty acids, number 1, for instance, yielding 0.92 per cent in that portion, while the balance contains but 0.27 per cent. This difference becomes more marked as germination progresses; it is only when the foot has come in complete contract with all the meat that an increase in fatty acids throughout the whole nut is observed, indicating that oil, to be in a condition for absorption, must be hydrolized. This hydrolysis may take place as the result of an enzyme in the foot, or be caused by one in the meat, which is dormant until rendered active by some product of metabolism in the foot. However, as I have stated in the previous chapter, it was not possible to prove by an increase in free acid the presence of any fat splitting enzyme in the coconut. Such an enzyme may exist, but under such conditions that any large excess of free acid must be used up by the growing plant before the process can continue.

A summary of the changes to be detected by chemical analysis of the growing coconut is as follows:

Oil is lost by the meat; it is not taken up as such by any other portion of the nut, but is either burned to furnish energy for the growing

plant or is split up, being transformed by progressive synthesis into sugar and finally to cellulose.

Sugar is lost by meat and milk, but a corresponding quantity is gained by the foot, the total amount in the nut remaining approximately the same.

A small amount of crude fiber is lost by the meat, but a much larger quantity is produced in the sprout and roots.

III. THE ACTION ON COPRA OF MICROÖRGANISMS IN PURE CULTURE.

It has been shown previously [3] that moist copra is readily attacked by microörganisms with consequent splitting up and destruction of the oil and it has also been proved that the action of such organisms is most pronounced when the copra has a water content of from 10 to 15 per cent. With this content of moisture the mold growth largely predominates over that of the bacteria. When much more water is present, and the bacteria are in excess of the molds, destruction of fat is greatly diminished. These observations led logically to the belief that hydrolysis of oil in copra was due to the action of molds alone, although the data available at the time the previous work was done did not exclude the possibility of symbiosis and interdependence in this fat-splitting process between molds and bacteria. Dr. Edwards, of the Biological Laboratory of this Bureau, undertook further work to settle this question definitely and in pursuing it separated as many different organisms as possible, some fifteen in all, from several samples of moldy copra and coconut meat, finally succeeding in isolating in pure cultures the majority of the growths present. As a culture medium he used sterilized coconut meat in most instances. The subsequent procedure was as follows:

Ten-gram samples of anhydrous copra were placed in large test tubes stoppered with cotton, and after the addition of 1.50 grams of water these were sterilized in an autoclave for half an hour. It was found by experiment that about 0.10 gram of water was taken up by the copra during sterilization, so that the samples thus prepared contained approximately 13.8 per cent of moisture, an amount which had been found previously to favor the growth of both molds and bacteria. The tubes were inoculated after sterilization with pure cultures of the organisms previously isolated, and allowed to stand at laboratory temperature (26° to 30°) for forty-one days. Cultures were then made from each tube. All tubes were dried to constant weight at 100° in order to determine the change in weight of the dry copra. The latter was next extracted with chloroform to determine oil and finally with hot water to take out the sugar, which was inverted and determined with Fehling's solution. The changes taking place in forty-one days are shown in the following table. Only those tubes which showed a good growth in this time and were proved by cultures to contain only one organism are noted.

[3] *This Journal* (1906), 1, 123.

TABLE II.—*The decomposition of copra by bacteria and molds.*

	Weight of dry copra—			Oil.			Sugar.		Undetermined.	
	At start.	After 41 days.	Gain (+) or loss (−).	Weight.	Gain (+) or loss (−).	Free fatty acid.	Weight.	Gain (+) or loss (−).	Nitrogen, coloring matter, cellulose, etc.	Gain (+) or loss (−).
	Gm.	*Gm.*	*Gm.*	*Gm.*	*Gm.*	*P. ct.*	*Gm.*	*Gm.*	*Gm.*	*Gm.*
Control of sterile copra	10.00	9.99	−0.01	6.94	0.00	0.20	0.45	0.00	2.60	0.00
Bacterium CB2, fairly good growth	10.00	10.05	+0.05	7.13	+0.19	0.36	0.48	+0.03	2.34	−0.26
Bacterium CB1, fairly good growth, copra somewhat darkened, slight sour odor	10.00	9.36	−0.64	6.64	−0.30	0.21	0.08	-0.37	2.64	+0.04
Bacterium W3+6, fairly good growth	10.00	9.98	−0.02	6.92	−0.02	0.20	0.50	+0.05	2.56	−0.04
Bacterium W5+6T, very slight growth	10.00	10.03	+0.03	6.91	−0.03	0.20	0.50	+0.05	2.62	+0.02
Mold W51, white, good growth, no odor	10.00	9.17	−0.83	6.06	−0.88	2.0	0.04	0.41	3.07	+0.47
Mold W3, dark green, good growth	10.00	9.13	−0.87	6.14	−0.80	3.8	0.07	−0.38	2.82	+0.22
Mold $W_13_11_1$, good growth in 6 days, ethereal odor, 9 days	10.00	8.84	−1.16	6.09	−0.85	24.7	0.02	− 0.43	2.73	+0.13
Mold *Aspergillus catenatus*, rapid, heavy growth after 15 days	10.00	9.37	−0.63	6.32	−0.62	8.3	0.05	−0.40	3.02	+0.42
Mold *Aspergillus flavus*, good growth in 7 days, ethereal odor after 15 days	10.00	9.13	−0.87	5.56	−1.38	12.0	0.06	−0.39	3.51	+0.91
Mold W3, 4, 5, good growth in 5 days, slight ethereal odor after 15 days	10.00	9.47	−0.53	6.24	−0.70	6.0	0.03	−0.42	3.20	+0.60

It was at first intended to identify each organism which was used experimentally, but this was found to be impracticable in this country where all literature is not available, except in the case of two molds, *Aspergillus catenatus* and *Aspergillus flavus*. It also seems probable that the majority of the other organism found in moldy copra in the Philippines are new and not yet described, and our mycological work is not yet far enough advanced to render descriptions of them possible. However, the main object of the experiments, namely the differentiation between mold and bacterial action on copra, has been accomplished. It is evident that in every tube containing an active mold culture, a decided loss in total weight (dry), ranging from 5 to 11 per cent of the original weight, occurs if the gain or loss in dry copra is first considered.

Only one bacterium, CB1, causes any appreciable loss in total weight. The molds destroy a certain percentage of the oil, and the greater proportion of the diminution in weight is due to this cause. These losses vary from 0.62 to 1.38 gram, which figures represent 8.9 to 19.9 per cent of the original weight of oil and they are in each case accompanied by hydrolysis of the oil to form fatty acids and glycerine, the final percentage of free acid varying from 2 in the case of "W51," to 24.7 per cent with "$W_1 3_1 1_1$."

There seems to be no relation between the percentage of free acid present and the total oil destroyed at the same time, the tubes containing the highest and the lowest percentage of free acid showing practically the same loss of oil. On the one hand, only one bacterium, "CB1," caused diminution of oil and this only to the extent of 0.3 gram, which is less than that brought about by the mold with the weakest action. Loss in oil is not accompanied by hydrolysis in this case. On the other hand, one bacterium, "CB2," appears even to have caused a slight gain in total oil. The sugar is almost completely destroyed by all molds and by bacterium "CB1." The *undetermined* matter shows a decided gain wherever mold action has taken place, this result being undoubtedly due to the weight of the mold itself.

Bacteria in all cases but one have produced no change in this constituent. "CB1" has caused a loss of 0.26 gram.

The results given above, when applied to the question of the diminution in value of commercial copra would render it certain that such copra, *if moldy,* has suffered a loss in total oil, of course not in all probability as great as I noticed in some cases (19.9 per cent), for my copras were placed under the most favorable conditions for the maximum of mold action, but nevertheless this change must amount to a sufficient quantity to be considered in the purchase of copra which has suffered from the action of molds.

Such materials undoubtedly can not give as good a yield of oil as others which have been carefully dried and preserved. However, another factor must also be considered. Poorly dried and preserved copras, if a sufficient quantity of water (above 15 per cent) is present, suffer from *bacterial* and not from *mold* action;[4] in which event no diminution of oil would be observed, but nevertheless bacteria so disintegrate and change the copra that a slimy, soft mass, difficult to work so as to procure pure oil reasonably free from acid, results. A bad odor also frequently accompanies such copras. In the Philippines a large amount of copra is dried by means of open fires in pits, the coconut meat is placed in bamboo gratings above, the fuel being the husks of the nuts. These

[4] This is clearly set forth in my paper on this subject in *This Journal* (1906), 1, 58.

conditions subject the materials more or less to the action of smoke, and it is not impossible that this procedure brings with it a slight antiseptic action which would tend to diminish the subsequent growth of organisms and work in favor of the final percentage of oil to be obtained in extraction. Nevertheless, the arguments are all in favor of preparing a clean, white, perfectly dried copra, which will not afford a medium for the growth of organisms unless the conditions of shipping which surround it are such as to allow of sufficient absorption of water after drying to facilitate mold growth.

SUMMARY.

Six different molds, any one of which is capable of hydrolyzing and destroying fat, have been isolated from among the many organisms found growing on rancid copra and coconut meat.

This fat destruction is part of the life process of the mold, and is independent of bacterial action, since it proceeds equally well in pure and in mixed cultures.

Copra which had been acted on by molds was found to have suffered an almost total loss of sugar.

The bacteria found on copra have very little effect on the quality or quantity of oil produced from it. A slight diminution in total weight of oil was found in only one case to be due to bacterial action. Practically their only effect is the production of a more or less disagreable "sour" odor and the disintegration of the meat.

It is good commercial practice to prepare only the best, white, perfectly dried copra.

IV. THE PRODUCTION OF FREE ACID IN COMMERCIAL COCONUT OIL ON LONG STANDING.

About 1 liter of crude coconut oil, freshly made from a rather poor quality of copra, was taken directly from a coconut-oil factory and allowed to stand in a large, wide-mouthed bottle for twenty-three days, until most of the turbid matter had settled out. During this time the free fatty acids had increased in percentage from 6.9 to 7.4,[5] or at the rate of about 8 per cent total increase per year. This rate of increase was fully double that which might be expected from a commercial oil of an initial acidity of 6.9 per cent, and it was thought possible that some abnormal influences were at work on this freshly prepared oil, which might or might not continue their effect on long standing; the logical idea being that the comparatively rapid splitting up of fat in copra by the action of molds

[5] This figure represents the clear portion of the oil. After shaking the bottle to obtain a representative sample together with sediment, etc., a figure of 7.6 per cent was obtained.

was being continued in the oil, either by portions of the mold carried over through the factory filters, or by enzymes which were expressed and which would find their way into the final product.

In order to determine if this supposition were correct, a number of 50-gram samples of the oil were subjected to different treatments, such as filtration to remove sediment and most of the water, the addition of antiseptic, sterilization by heat or by a combination of all three of the above processes. The oils were heated at a temperature of 100° in a water oven for two hours; ordinary quantitative filter paper was used for filtration. Two samples from each treatment were prepared, one being kept in a 100 cubic centimeter bottle half full, the other in a 50 cubic centimeter bottle filled to the neck. Unless otherwise stated, samples were sealed with paraffin and kept in the light. One sample, in the case of numbers 7 and 8, was kept in the light in 100 cubic centimeter Erlenmeyer flasks with sterilized cotton plugs, where air and light might be expected to play the leading part in any change produced; the other sample was kept in a wooden box covered with black paper.

The following table shows the change in acidity during a period of two years:

TABLE III.—*Change in acidity of coconut oil standing under different conditions for two years.*

No.	Description of oil.	Description of package and condition.	Free fatty acid at start of experiment.	Free fatty acid after 1 year.	Increase during the first year.	Free fatty acid after 2 years.	Increase during the second year.	Total increase in 2 years.
1	From original bottle unheated, unfiltered, no antiseptic.	a. Small bottle	7.6	11.2	3.6	11.6	0.4	4.0
		b. Large bottle	7.6	11.0	3.4	13.4	2.4	5.8
2	Unheated, *filtered*, no antiseptic	a. Small bottle	7.4	8.8	1.4	9.7	0.9	2.3
		b. Large bottle	7.4	8.8	1.4	11.2	2.4	3.8
3	Unheated, unfiltered, *+0.05 per cent chloral.*	a. Small bottle	7.6	9.6	2.0	10.9	1.3	3.3
		b. Large bottle	7.6	9.2	1.6	11.9	2.7	4.3
4	Unheated, *filtered, +0.05 per cent chloral.*	a. Small bottle	7.4	8.7	1.3	9.5	0.8	2.1
		b. Large bottle	7.4	8.7	1.3	10.2	1.5	2.8
5	*Heated*, unfiltered, *+0.05 per cent chloral.*	a. Small bottle	7.6	8.9	1.3	9.9	1.0	2.3
		b. Large bottle	7.6	9.0	1.4	11.2	2.2	3.6
6	*Heated, filtered, +0.05 per cent chloral.*	a. Small bottle	7.4	8.2	0.8	8.8	0.6	1.4
		b. Large bottle	7.4	8.9	1.5	10.4	1.5	3.0
7	*Heated*, unfiltered, *+0.05 per cent chloral*, kept in Ehrlenmeyer flask with cotton stopper.	a. In light	7.4	9.6	2.0	13.0	3.4	5.4
		b. In dark	7.4	9.6	2.0	[a]12.8	3.2	5.2
8	*Heated, filtered, +0.05 per cent chloral*, kept same as number 7.	a. In light	7.4	11.0	3.6	15.0	4.0	7.6
		b. In dark	7.4	11.6	4.2	[a]15.9	4.3	8.5

[a] Since no increase in acidity due to the action of light could be observed after one year, the samples previously kept in the dark were taken out and placed alongside the others serving simply as a check on the determinations.

It is necessary for the interpretation of these results to consider the many factors which may enter into the decomposition of a freshly prepared, commercial coconut oil.

First, we may have present fat-splitting molds, albuminoids, sugar and water, which cause the turbid appearance of commercial oils. It has been shown in a previous paper[6] that mold action on copra is the principal factor in determining the initial acidity of an oil, and that these same molds in the presence of sufficient nutritive matter may effect the rapid decomposition of even a pure oil. *Second*, soluble or insoluble enzymes produced by these molds may be the cause of the rise in free fatty acid. *Third*, surface oxidation by the air, possibly assisted by light, may take part in the decomposition. This surface oxidation is always accompanied by a pungent, disagreeable odor, and the formation of aldehydes and peroxides. *Fourth*, simple hydrolysis by heat and moisture may be a factor.

Considering first sample number 1 of this series, it is evident that 1-b, the sample in the large bottle, may be subject to any one or all of the foregoing factors causing increase of acidity, while 1-a, being in a practically full bottle, may be affected by any influence except that of oxidation by the air. Any marked increase in acidity, then, of 1-b over 1-a would be due to surface oxidation. By reference to the table we find that during the first year there has been practically no difference in the rate of increase of acidity between 1-a and 1-b, which show respectively a gain of 3.6 and 3.4 per cent. The second year, however, indicates a decidedly different condition. While 1-a has only gained 0.4 per cent free acid, 1-b has increased 2.4 per cent, leaving a difference of 2 per cent which can only be due, aside from experimental error and an individual variation in the samples, that should at most amount to no more than a few tenths of a per cent, to surface oxidation by the air. The question naturally arises, why should a period of two years be required for this difference to show itself? This can be accounted for by two theories: *First*, the presence of molds and of nutritive bodies such as sugar and albumen, which would be in the oil in larger quantity in the first year than in the second, is not favorable to the formation of peroxides of the fatty acids, a fact I have previously noted in testing pure and commercial oils for peroxides and aldehydes;[7] *second*, it is possible that this inhibiting effect may be mutual, so that oxidation once started would tend to kill off or check mold or enzyme activity in 1-b sooner than this activity would naturally cease through lack of nutriment in 1-a. In either case, the result would be the same and the combined effect of the

[6] *This Journal* (1906), **1**, 139.
[7] *Loc. cit.*, 139.

two processes, each ending ultimately in the production of free acid, might be less than either of them working singly. The probabilities are that oxidation does not set in until most of the nutritive substances present in the oil are used up, thus it would be natural to expect that for a certain period of time no difference in the rate of acidification of an oil, due to the size of the container, would be observed.

Sample number 3 was filtered, removing molds, albuminous matter and any enzymes insoluble in oil, together with most of the water. During the first year an increase in acidity of 1.4 per cent was noted. The difference between this figure and 3.6 per cent, the increase of 1-a for a corresponding time, gives 2.2 per cent which may be attributed to molds and insoluble enzymes. Practically no difference, due to size of bottle, is observed in number 2 as well as in nearly all the other samples, during the first year, although it is quite marked at the end of the second year. Number 3 differs from number 1 only in containing a small amount of antiseptic. It shows 1.6 per cent less increase during the first year than number 1. This can be due only to inhibition of molds. During the second year 3-a has increased 0.9 per cent more than 1-a, a fact for which I can find no explanation, except that during the second year some surface oxidation may have taken place, even in the small bottles. Five cubic centimeters of oil had been removed for titration at the end of the first year, thus leaving a small air space. This being the case, somewhat wider variation in acidity might be expected. The figure of 0.4 increase for the second year in the case of number 1-a seems exceptionally low, compared with the other samples during this period. 3-a has increased only a trifle more in acidity as compared with 2-a, thus proving that the addition of antiseptic has about the same effect as filtration and that most of the difference in behavior of a filtered and an unfiltered oil is due to the removal of molds and insoluble enzymes. Number 4 was filtered and treated with antiseptic with results which practically correspond with those of 2 and 3. Filtration appears to be slightly more efficient than adding antiseptic. It is quite possible that chloral in the strength used does not have an immediately fatal effect on fat splitting molds, although it certainly inhibits their action to a very marked extent.

Numbers 5 and 6 have both been heated at 100° and treated with antiseptic, thus eliminating mold and enzyme action, and in the case of full bottles leaving only the factor of hydrolysis to be considered. As would naturally be expected, the filtered sample, 6-a, has increased in total acidity considerably less than 5-a, from which the water was not removed. Only number 6 of the whole series shows practically the same difference at the end of each year between the full and the half full

bottles. The slight, but regular, increase in acidity of 6-a is probably due to the hydrolytic action of a trace of water not removed by filtration, combined with the free fatty acids already present. Some slight oxidation also may have taken place, as the bottle was not absolutely free from air.

Numbers 7 and 8, sterilized and kept under antiseptic conditions in Erlenmeyer flasks, with a large oil surface exposed and free access of air through the cotton plugs, practically doubled their percentage of free acid in two years. The filtered samples of number 8 show considerably more increase than the unfiltered oils numbered 7, a fact which tends to confirm my belief that as a general rule the freer an oil is from moisture and impurities the more quickly is it subject to oxidation when exposed to the air. The samples kept in the light have not increased in acidity any more than those kept in the dark, in fact, 8-b at the end of one year contains 0.6 per cent more free acid than 8-a.

In view of this latter work, indicating the considerable variation in acid content of the same oil which may be brought about by different sized containers with consequently varying amounts of oil exposed to the air, it was decided to bring to a close the series of oils described in a previous paper [8] and which were set aside to determine the amount of free acid which might be produced on standing, since after the first year, most of the further increase in acidity would be dependent to a very large extent upon the amount of oil surface exposed to air in the bottles. No attempt was made at the time when these samples were prepared to exclude oxidation by keeping them in filled bottles, and with few exceptions no record was kept of the quantity of oil in a bottle, so that wide variations in acidity after the first year were to be expected. For convenience, a description of the oils as first made is reprinted here, together with a table giving their increase in free fatty acid from the time of their preparation up to the present date.

DESCRIPTION OF OILS USED AND DESCRIBED IN TABLE IV.

(A) Expressed oil from vacuum-dried copra. Has been heated for two hours at 100° and filtered twice through paper. A light-colored, clear oil with the characteristic coconut taste and odor.

(B) An oil similar in every respect to "A" except that it was prepared from copra dried at 80° to 90°, without vacuum.

(1) Fresh coconut meat grated and dried at 80° to 90° on August 16, 1904; was allowed to stand in a covered specimen jar until March 11, 1905. At that time it was still of a pleasant odor and taste, although both odor and taste were not quite as good as when the specimen was freshly prepared. No mold

[8] *Ibid.*, 118.

growth was present. A sample of oil was expressed from a portion of this copra by using a hydraulic press with a final pressure of 450 kilograms per square centimeter. This oil, after filtration, was of a light yellow color and it was of a pleasant, although slightly burnt, odor and taste.

(2) Oil number 1 was heated at 100° for three hours, while at the same time a current of air in a partial vacuum was passed through it. This process leaves the color and free acid unchanged, but removes almost all of the burnt odor, leaving a bland, almost tasteless, oil.

(3) An oil from the same copra as numbers 1 and 2, but prepared by extraction with petroleum ether. Afterwards it was treated in the same manner as number 2. It differs from numbers 1 and 2 in being practically colorless.

(4) Commercial coconut oil treated with alcohol and animal charcoal and then filtered; the alcohol was afterwards distilled and recovered. This oil was rather unpleasant to the taste, but it had no odor.

(5) Commercial coconut oil treated with live steam; this removes the odor, but the unpleasant taste remains.

(6) Fresh meat, ground and dried in vacuum at 70° to 80°. The oil was expressed and once filtered; it possessed a very pleasant, coconut-like odor and taste. It still contained a considerable amount of sediment.

(7) Coconuts cut in halves and dried in vacuum at 75° to 85°. The oil expressed and filtered twice. It had a very pleasant odor and taste.

(8) The same oil as number 7, heated at 100° for one and one-half hours and filtered hot.

(9) The same as number 7, heated at 100° for one and one-half hours, while at the same time a current of air was passed through the oil under partial vacuum. Filtered hot and bottled.

(10) Fresh coconut meat, ground and pressed in a hand press to remove most of the milk. Afterwards this meat was dried completely by spreading it in the sun for about five hours. The oil expressed from this copra was almost water white and without taste and odor.

(11) Coconuts split in halves and dried in the sun for five days. Ground and expressed. Yielded a cloudy, slight colored oil, very hard to filter, with a peculiar, but not unpleasant, taste and odor. This sample was strained through cloth but not filtered.

(12) Same as No. 11, strained and filtered slowly through paper.

(13) Same as number 11, heated at 100° for two hours and filtered through paper.

(14) Fresh nuts, split in halves and allowed to stand during one week in the air at room temperature (about 30°). A vigorous mold growth and an unpleasant odor developed. This moldy meat was dried in a vacuum and the oil was expressed. This was highly colored and was rather unpleasant to taste and smell.

(15) Commercial coconut oil shaken with 2 per cent of solid calcium oxide (burned lime), heated to 100° and filtered. The filtrate was treated with animal charcoal and again filtered; there resulted a colorless oil which was very free from an unpleasant odor or taste.

(16) The same copra as that used for number 1; was allowed to stand one month longer in an open jar, then expressed.

(17) Oil expressed from vacuum-dried copra which had stood for one month exposed to the air; the oil was heated to 100° and filtered.

(18) Expressed from sun-dried copra and treated in the same manner as number 17. Both of these samples were of as pleasant a taste as oils from fresh copra.

(19) Vacuum-dried copra which had stood in a closed desiccator over water for one month, and which had accumulated a very decided growth of mold. It was dried for one hour and expressed. The oil had a considerable color and was slightly unpleasant as to taste and odor. Heated to 100° and filtered.

(20) Sun-dried copra treated in the same way as number 19. Yielded an oil somewhat darker in color but otherwise much the same as number 19. Filtered without heat.

(21) Same as number 20, heated to 100° before filtering.

(22) The same copra as that used for samples 1 and 16 was allowed to stand for three weeks over water and for one week in air, and then dried and pressed. A vigorous mold growth appeared in the copra and a peculiar ethereal odor was apparent. The oil itself was of a light-yellow color, with a pungent, rather unpleasant, odor and an extremely disagreeable taste.

(23) Expressed from commercial copra, first quality, sun dried, Tacloban, Leyte. The unfiltered oil is dark colored and cloudy, depositing a black sediment.

(24) Same as number 23, filtered. Almost colorless.

(25) Expressed from commercial copra, grill dried, Laguna (second quality). Not filtered.

(26) Same as number 25, filtered. Light yellow in color.

(27) Expressed from commercial copra, grill dried, Romblon (considered second quality). The filtered oil is light yellow color.

(28) Expressed from commercial copra, first quality, sun dried, Iloilo. The filtered oil is light yellow in color.

(29) "Langis" coconut oil, prepared by the customary native process of grating the fresh meat, exhausting it repeatedly with water, and boiling down the emulsion thus obtained until it is nearly dry. The oil is then poured off from the brown coagulum which sinks to the bottom of the vessel. A freshly prepared oil, isolated in this manner, is very light in color and it possesses a decidedly pleasant coconut odor and taste. Before filtration it is more or less turbid, owing to the presence of a small amount of water and of albuminoids.

(30) Same as number 29, filtered. The oil is water white.

(31) Best grade commercial coconut oil, probably made from fresh meat. It is light colored, but very turbid and contains considerable water and suspended matter.

(32) Commercial coconut oil, probably made from copra. Very clear but highly colored.

(33) Commercial coconut oil, Manila. Probably made from fresh meat. It contained considerable suspended matter and water.

(34) Commercial coconut oil, Cebu. A highly colored "rancid" oil. Considerable sediment in the bottom of the bottle.

(35) Commercial coconut oil, Tayabas. A highly colored rancid oil made from copra. It is only a few months old.

TABLE IV.—*Percentage free fatty acid (as oleïc).*

No.	At start.	Two months.	Four months.	Six months.	One year.[a]	Three years.
A	0.06	0.06	0.09	0.60	2.6	9.6
B	0.06	0.06	0.08	[b]0.48	[c]2.3 [d]0.14	8.9 0.37
1	1.2	1.3	1.5	1.9	3.1	9.4
2	1.2	1.5	1.5	1.7	2.1	3.7
3	1.4	1.6	2.1	2.6	3.9	----------
4	5.3	----------	5.9	6.1	6.8	9.0
5	5.5	----------	----------	7.6	10.1	28.2
6	0.10	0.16	0.19	0.30	0.53	1.9
7	0.16	0.18	0.19	0.27	0.39	1.0
8	0.16	0.14	0.19	0.30	0.40	0.93
9	0.16	0.16	0.18	0.25	0.35	0.93
10	0.16	0.16	0.21	0.28	0.54	1.5
11	0.13	0.18	0.25	0.28	0.43	3.5
12	0.13	0.10	0.10	0.14	0.28	1.0
13	0.13	0.09	0.09	0.15	0.28	1.1
14	3.5	3.7	4.0	4.3	4.7	5.7
15	0.32	----------	0.88	----------	3.3	----------
16	1.6	1.7	2.0	----------	4.4	----------
17	0.09	0.09	0.14	0.16	0.25	0.81
18	0.16	0.18	0.25	0.27	0.44	0.82
19	1.18	1.14	1.34	1.58	2.0	3.5
20	0.69	0.69	0.74	0.85	1.1	2.7
21	0.69	0.69	0.74	0.82	1.1	2.0
22	23.3	----------	----------	----------	30.0	----------
23	1.4	1.6	1.8	2.0	2.5	3.9
24	1.4	1.5	1.7	1.8	2.5	6.0
25	2.6	3.4	3.6	3.9	4.8	----------
26	2.6	2.6	3.1	3.5	4.5	----------
27	2.1	2.4	2.5	2.8	3.1	4.2
28	3.0	3.5	4.0	4.7	6.1	11.4
29	0.08	0.38	0.60	0.69	1.4	3.9
30	0.08	0.13	0.16	0.19	0.80	----------
31	2.0	2.9	----------	----------	7.5	----------
32	6.8	7.5	7.9	8.1	9.2	16.1
33	5.5	----------	6.9	7.2	8.2	16.5
34	8.7	----------	10.2	11.0	13.8	----------
35	5.0	5.5	----------	----------	8.2	----------

[a] The greater part of the titrations at this period were made by Mr. L. A. Salinger of this Bureau who kindly continued the series during my absence from the Bureau.

[b] This oil was kept in a large bottle. A sample in a small bottle showed an acidity of only 0.09 a this time.

[c] Large bottle.

[d] Small bottle.

The most apparent fact which is noted on examining these tables is the proportionately large increase in free acid after the first year.

In some samples this change is so great and so unexpected as to appear at first glance inexplicable, but in such cases I have nearly always

been able to detect some abnormality in the conditions under which the sample had been kept. For instance, numbers 1 and 2, samples of identically the same oil, the only difference between which lay in the fact that number 2 had been treated for three hours with a current of dry air to deodorize it, increased in free acid in practically the same ratio during the first six months; at the end of a year number 1 contains only 1 per cent more acid than number 2, but after three years shows 9.4 per cent as against 3.7 per cent in number 2. On examining the bottles in which these samples were kept I noticed that number 1, of which a considerable quantity had been prepared at the start, was still in the original 250 cubic centimeter bottle in which it had first been placed. About half of this oil had afterwards been taken out for the preparation of number 2, and filled into a 100 cubic centimeter bottle. This difference in the size of bottle, then, with a corresponding different surface exposed to oxidation, must account for the 5.7 per cent excess of free acid of number 1 over number 2.

A still more striking example of the influence or surface oxidation is afforded by sample B. This was an exceptionally pure oil, sterile and freed as far as possible from impurities by repeated filtration. One portion of about 25 cubic centimeters was transferred to a small bottle nearly, but not quite, filled, shortly after preparation, while in the original 500 cubic centimeter bottle there remained at the end of three years about 20 cubic centimeters of oil. The latter sample has increased in acidity 8.8 per cent in three years, while the former, from which air was nearly completely excluded has gained only 0.31 per cent free acid in the same time. Sample number 5, a commercial oil which changed from 5.5 per cent free acid to 28.2 per cent, had originally been treated with live steam to remove its unpleasant odor, and decanted into a bottle without filtering out all the water of condensation from the steam. When the final titration was made there remained between 5 and 10 cubic centimeters of oil, together with considerable water, so that hydrolysis by water undoubtedly had much to do with the large amount of free acid developed.

It will be noted that oxidation once started proceeds more rapidly in oil already having a large free acid content than it does in those comparatively low in acidity (compare numbers 6 to 13 and 17 to 21 with the commercial oils from number 23 on). Exceptions to this rule are, as above stated, due to abnormal conditions of storage.

The behavior of these oils during the period prior to the appearance of oxidation has been discussed in a previous paper and no new data have been brought out by longer storage which do not tend to confirm the conclusions drawn at that time.

CONCLUSIONS.

The deterioration of a freshly prepared commercial coconut oil is produced by at least three entirely independent processes and may be divided into two distinct periods of time.

The first, rapid splitting up of the fat, beginning immediately after its expression from copra and continuing for several months up to a year or more according to the nutrive matter present, is occasioned by molds which are either pressed out with the oil together with sufficient sugars and albuminoids for their growth, or, in the case of hot pressed oils, enter the freshly prepared oil from the air. This action continues as long as sufficient nutritive material for mold growth remains in the oil. It may be completely checked by filtration, preferable after heating to 100° C. more thoroughly to coagulate albuminoids and to destroy any enzymes already secreted by the molds.

Toward the end of this first period, oxidation by the air sets in and may continue indefinitely. The rate of this process depends upon the amount of surface exposed to the air, compared with the total volume of oil, and may in extreme cases cause an exceedingly rapid deterioration. It may be entirely prevented by storing the oil in completely filled receptacles, impervious to air.

Along with the two above-mentioned processes, a slight hydrolysis due to heat, moisture and free acids already present is constantly taking place. It may be reduced considerably by filtration, which removes most of the water, together with the organic impurities.

There is reason to believe that some hydrolysis is brought about by enzymes produced by the molds, as unheated oils which have been filtered and rendered antiseptic increase in acidity somewhat more rapidly than do heated ones under the same conditions. However, this distinction is not so apparent after the first year.

Light has apparently no effect on the oxidation by air of coconut oil.

PORTLAND CEMENT TESTING.

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INTRODUCTION.

This paper is devoted to a discussion of modern cement specifications and we have endeavored to point out many reasons why they do not exclude the personal error that is experienced by all testers working under them. Simple methods and precautions necessary to reduce this variation have been suggested. Throughout the discussion, the effects of the requirements of cement specifications, the difference possible in manipulation and the consequent variations in the results obtained have been illustrated. Certain powerful climatic influences that tropical conditions may exert upon cement are also discussed, and the last chapter suggests the characteristics which a cement should have to give the greatest efficiency under tropical influences.

SPECIFICATIONS.

The "value of standard specifications to the engineer, the consumer, and the country at large is as great as their value to the manufacturer. A standard specification, provided it is both equitable and safe, cheapens the product, insures quicker deliveries and acts as a powerful regulator to the industries affected. * * * *The danger of a fixed standard of any kind lies in its becoming unprogressive and following behind the demands of the time.*"[1]

The last sentence should be especially emphasized. All official cement testing in the Philippines at present is done under the United States Army Engineer Specifications of 1902. No change has been made in these specifications in the last six years despite the great amount of work which has been done upon the physical and chemical properties of Portland cement in recent times, and, in the light of experience, it has been found that these specifications could certainly be improved. This unprogressive tendency is, perhaps, due to the inertia inherent in all committee work. Each individual member has fixed ideas on certain questions, or on the results of certain personal experiences. As one writer

[1] Editorial: *Eng. News* (1904), **51**, 612. (Italics supplied.)

puts it: "We are all disposed to argue somewhat on the basis of our prejudices or to refute others because of the prejudices which we associate with them. * * * Therefore it is difficult for us to arrive at conclusions purely by the light of reason, and to deal with every syllogism from its premises to its conclusions."

However, the American Society of Civil Engineers and the American Society for Testing Materials are constantly working to improve their cement specifications and these specifications will soon be adopted by the Government of the Philippine Islands for all civil and municipal work. They have accomplished much towards establishing a more practical, impartial and comprehensive system of testing. Yet "notwithstanding that so much has been done towards unification of methods, it may never be possible to determine accurately the value of one cement as compared with another tested in a different laboratory".[2] "Experience since the report of the committee was made has shown that the difficulties in the way of uniformity in such tests are much greater then was then imagined. The variation in the results of tensile strength between the work of different experienced operators working by the same method and upon the same material are frequently very large and often make all the difference between rejected and accepted cement. Differences in tensile strength with neat cement of 40 to 60 per cent are not uncommon, while for sand mortar they are much greater." [3]

At present all standard specifications leave much to be desired. A Government committee appointed to investigate the quality of a certain brand of cement, after much consultation with engineers, chemists, contractors and manufucturers, introduced its final report with these remarks:

"There are no standard specifications which are regarded as absolutely correct. All tests are approximations and must be interpreted in accordance with the specifications in use, and with due regard to the purpose for which the cement will be used.

"There is no practical difference between the qualities and properties of a rejected and of an accepted cement in the immediate vicinity of the limits set by specifications." [4]

It follows that the engineer may be in much doubt as to whether to reject or accept a cement.

"It must be recognized, however, that cement specifications are not for average results, but are intended to cover the lowest limit which can be allowed in the work and to provide for lack of uniformity in testing as well as in real quality." [5]

[2] Sabin, Louis Carlton: Cement and Concrete. New York (1905), 30.

[3] Spalding, Frederick C.: Hydraulic Cement. New York (1904), 115.

[4] Final report of cement investigation committee appointed by Executive Order No. 60, 1907.—The Government of the Philippine Islands.

[5] Taylor and Thompson: Concrete, Plain and Reinforced. New York (1907), 99.

Such a conclusion may be satisfactory to the engineer, but should the tests be close to the margin specified for acceptance, the selling agent is sure to protest and order a retest of the material. He may allow the original tester to retest the cement, or he may send the samples to one of the many commercial laboratories whose reputation for high results in cement testing is well established. The retesting may produce satisfactory results in either case owing to the weakness of all cement specifications. "It is not to be inferred however that the highest results are necessarily the outcome of the greatest skill. As a rule the most expert and reliable operators get only moderate strength for the best material." [6]

Such a condition of cement testing is very deplorable. Unless specifications guarantee an accuracy within 10 per cent, the greatest efficiency of a cement laboratory is also lost, as the mere mechanical routine testing of various brands of cement should be the least important part of its work and satisfactorily to accomplish the more important object, namely a systematic study of the peculiar effects of climatic conditions upon them, a variation factor of not more than 10 per cent is essential.

Sabin states that "the chief object of testing cement is to arrange the various products in their true order of merit. Cement is at present used in a very crude way and it is only in exceptional cases that poor quality of material may be detected in the completed structure. This is sufficient reason why so few failures can be found in cement work which may be attributed to the poor quality of the cement. But in the more economical manner in which the material is, even now, being used, it is absolutely essential to know what its future behavior will be." [7]

We believe that the inefficiency of all American specifications lies in the fact that they do not outline sufficiently in detail the minor considerations and operations, and that to these minor details, owing to the peculiar and sensitive character of cement, is readily attributed a possible variation in the results of testing of 30 to 40 per cent. There are certain qualities in cement manipulation that can not be controlled, such as the size, shape and intermingling of crystals, nonhomogeneous voids in sand briquettes, unequal action of the water upon the hardening of briquettes, etc., but we believe that by far the greater variation is caused by the different manner in which different laboratories interpret the minor details of manipulation and treatment; and we also believe that if specifications were more explicit in this respect it would be safe to predict that different laboratories would agree within 10 per cent. This assumption is supported by the well-known fact that the system of the individual laboratory usually produces fairly uniform results, but a comparison between different laboratories which differ only in those details not explicitly treated in the specifications, often shows the most

[6] Spalding, Frederick C.: Hydraulic Cement. New York (1904), 160.

[7] Cement and Concrete. New York (1905), 82.

startling inconsistencies. To be more explicit, we will give, for example, the following tests made under the Army Specifications for 1902:

Two operators of considerable experience were ordered to test according to these specifications a shipment of 1,000 barrels of cement under dispute. Fifty samples, each representing one barrel, were taken at random, tested, and the figures tabulated as shown by the accompanying diagrams numbers 1 and 2 and by Table I.

TABLE I.—*Showing the variations from the mean of 200 breaks of each of the four sets of briquettes made by the testers.*

Tester.	Neat (200 each).		Mortar, 1 to 3 (200 each).	
	7-day.	28-day.	7-day.	28-day.
A	502.4	601.8	143	220.6
B	566.8	641.3	164	235.3
Mean	534.6	621.6	153.5	228.0
Difference	32.2	19.8	10.5	7.4
Per cent	±6.0	±3.2	6.8	3.2

Increase from 7 to 28 day tests.

	Neat.[a]		Mortar, 1 to 3.[b]	
	A.	B.	A.	B.
Pounds	99.4	74.4	77.6	71.3
Per cent	19.8	13.1	54.3	43.5

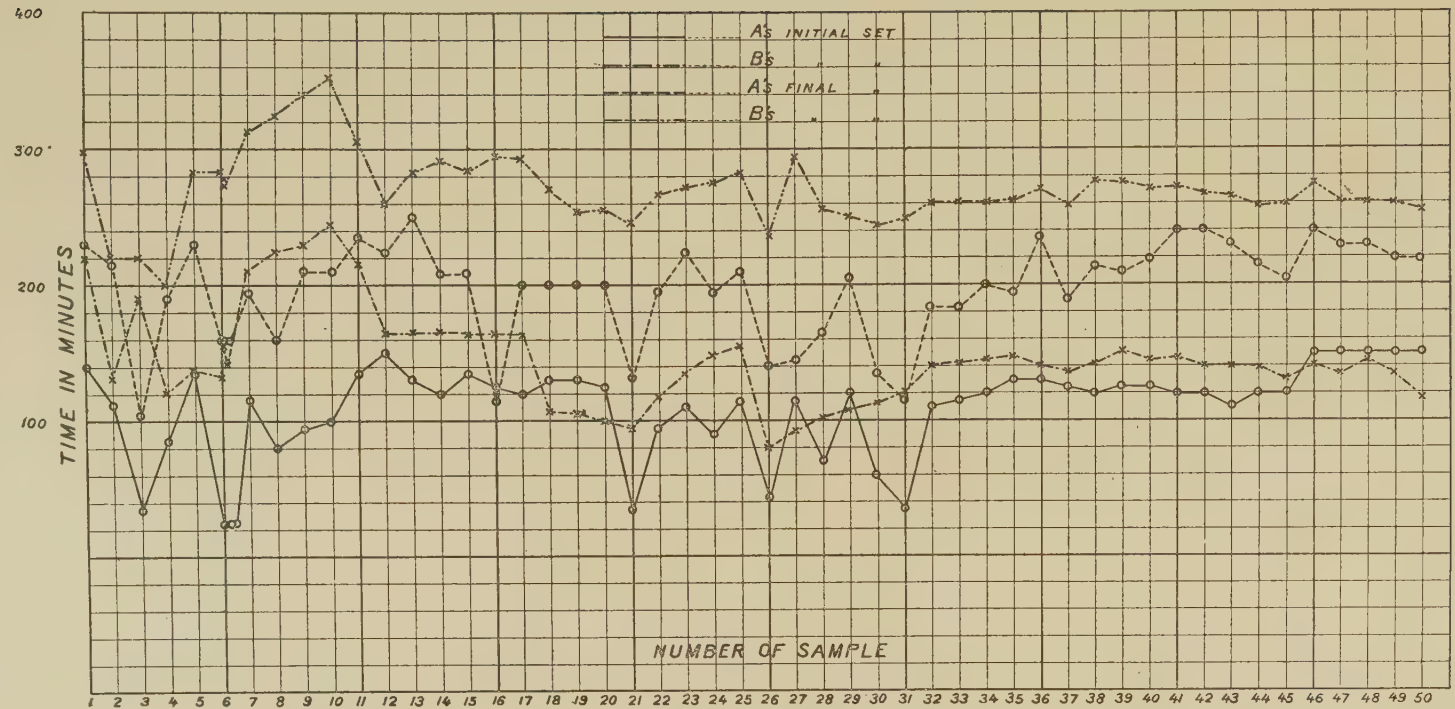
[a] Increase desired by specifications; 20 per cent.
[b] Increase desired by specifications; 57 per cent.

The fineness (through 100-mesh sieve) varied from 94.2 to 97.3.

The specific gravity dried at 110° in all cases, was below 3.08 and ranged from 3.02 to 3.07.

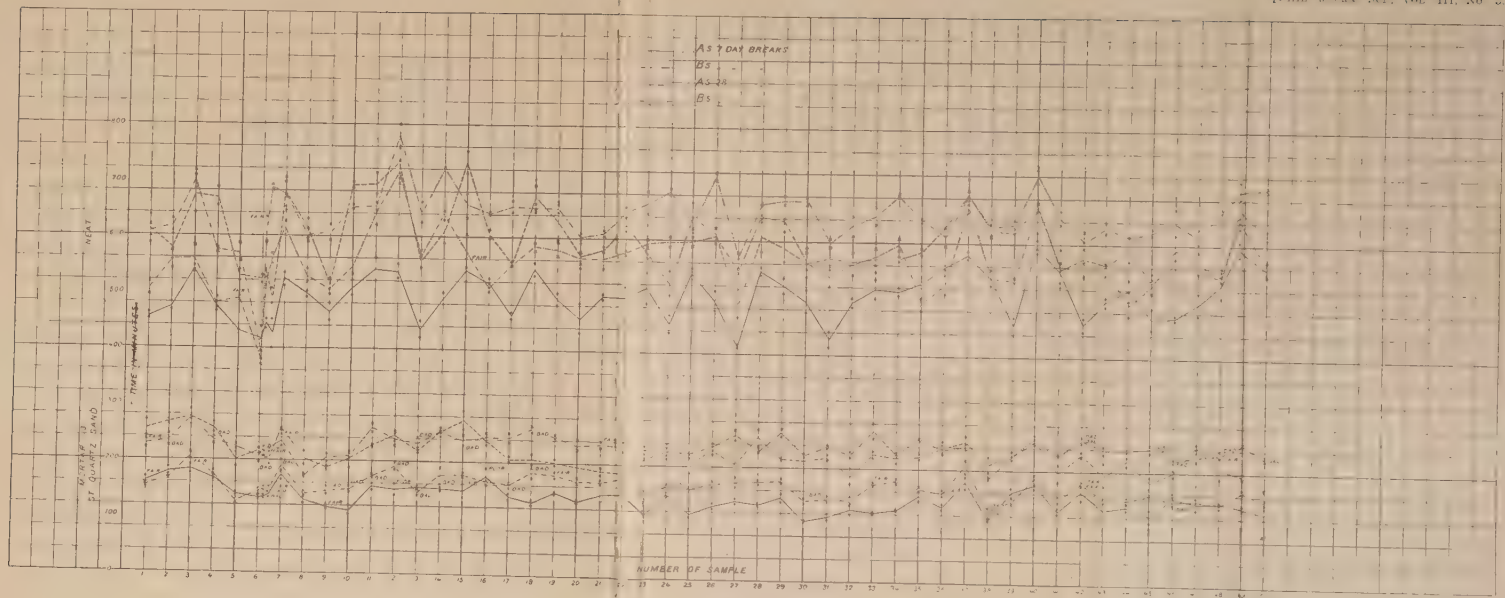
Space will not permit of discussion in detail of the methods used by each tester, except to say that A used the automatic tamper described below and applied the blows differently than did B, who used the ordinary tamper; A's briquettes were placed in a wet closet, B used the damp cloth; A's briquettes were also always under water, kept running for a few hours each day; B siphoned the water from the pans and then refilled them, thus exposing the briquettes to air for about 10 minutes each time. All these differences were in accordance with specifications, as the minor details of testing were indefinite enough to allow them.

One operator, A, always obtained lower results on an average than B, but B did not show the gain in strength between the 7 and 28 day tests that the cement was capable of. Evidently, B's system gave abnormally high 7-day tests, and therefore 28-day breaks showed little increase. However, notwithstanding these differences, the variation between the samples themselves is also clearly evident.



TIME OF SETTING

DIAGRAM NO. 1.



TENSILE STRENGTH

Diagram No. 2.

The diagram calls attention to the lack of uniformity in the results attained in each sample. The differences in the tensile strength are not only between the two testers, but also brought out by the same individual: those in the increase of strength with age, the failure on the part of one tester to obtain good breaks in many instances, and the great variation in the time of setting, are all apparent; yet both operators worked carefully and in strict accordance with the United States Army specifications. The committee in charge, after thoroughly investigating the methods of the two operators, reported as follows:

"The methods followed by each cement tester differ slightly in certain details, but the differences are not regarded by the committee as important or as in violation of the purport of the specifications; and the results obtained in each laboratory are regarded as fair, equitable and reasonable to both manufacturer and user." [8]

Even careful inspection of these charts would probably convince almost anyone that the tests, as they stand, are practically useless; that one of these testers, or even both, were inefficient; or that the cement itself was of a most peculiar quality. However, as will be shown, the whole inconsistency was due to a cause the elimination of which the specifications do not even mention. It appears that the work of the testers for time of setting, 28-day neat and sand strength, and specific gravity determinations, was accurate and true to the quality of the cement at the time it was tested. The cause of the great variability so evident in diagrams numbers 1 and 2, was due to the fact that each tester worked the cement after it had undergone various degrees of exposure to aëration, and that the influence of this factor produced very marked changes in the quality of the cement.

THE EFFECTS OF AËRATION.

Most of the cement specifications now in use devote considerable space to the manner in which the samples should be taken, but they all neglect to state how these samples shall be stored and preserved until tested. As a result, they may be sent to the laboratory in wooden or paper boxes, paper or cloth bags, tin cans, galvanized-iron cans, glass jars, etc. The cloth and paper may be thin or thick, and the cans, jars and boxes may have tightly or loosely fitting covers, or even no covers at all. These samples may be tested as soon as they are received at the laboratory or, owing to the amount of routine work already on hand, they may stand for some days before being worked. As a result of all these conditions the cement may have been subjected to unequal aëration and its characteristics changed accordingly; this change has often been sufficient to alter the resulting tests from satisfactory to unsatisfactory.

[8] Final report of cement investigation committee appointed by Executive Order No. 60, 1907.—The Government of the Philippine Islands.

The literature on the subject of cement is filled with information on the effects of aëration.[9] Cements high in lime or those which are "unsound" due to the presence of free lime, are improved by exposure to the air, but cements high in alumina, especially if lightly burned, are apt to become quick setting and otherwise dangerous under the same treatment. This is especially true in the tropics as "aluminous cements are readily subject to alteration in surroundings exposed to alternate dryness and humidity and also when exposed to a high temperature." [10]

Cements are encountered, the fineness and soundness of which may be very satisfactory throughout, but the specific gravity, time of setting and tensile strength (the 1 to 3 mortar especially) may vary from one extreme to the other. None of the pats may warp or disintegrate, even during steam and air exposures, so that perfect soundness may be a characteristic of such material. In fact, it is possible for a pat to remain at a red heat for several hours before it disintegrates in any marked decree. Cement of this class, according to chemical analysis made from time to time, proved itself to have a uniform composition in all respects except the loss on ignition, which varied from 1 to 6 per cent. The silica content was uniformly low and the alumina and iron high. It is hardly necessary to add that every known precaution was taken to secure uniform results.

Experience in this laboratory has demonstrated that in most instances variations such as those mentioned are encountered in cement samples which have been received in thin paper bags, or which had otherwise been exposed to the air; and that cement received for testing in closely covered cans and boxes and not subsequently exposed to the air, usually gave very acceptable, uniformly good results. These conclusions are emphasized by the following tables:

TABLE II.—*Characteristic examples of tests of cement stored in cans.*[11]

Sample No.	Mortar, 1 to 3.		Sample No.	Mortar, 1 to 3.	
	7-day.	28-day.		7-day.	28-day.
D5-2	240	289	BB13	225	307
D5-4	210	265	BB14	238	295
D5-6	210	305	BB15	205	299
D5-8	193	300	BB16	212	260
D5-10	210	315	BB17	248	288

[9] Meade: *Chem. Eng.* (1907), 5, 341; Taylor and Thompson: Concrete, Plain and Reinforced, New York (1907), 62; Spalding, Frederick C.: Hydraulic Cement, New York (1904), 4, 56, 80; Candlot, M.: Cement et Chaux Hydrauliques, Paris, 1891.

[10] Spalding, Frederick C.: Hydraulic Cement. New York (1904), 81.

[11] The setting time in all of these cements was satisfactory and uniform.

TABLE III.—*Variations in the same brand of cement received in paper bags.*

[Mortar, 1 to 3.]

Sample No.	Highest.		Sample No.	Average.		Sample No.	Lowest.	
	7-day.	28-day.		7-day.	28-day.		7-day.	28-day.
D1-1	187	269	C5-1	168	260	B9-1	126	194
D1-2	179	259	C5-2	141	214	B9-2	166	240
D1-3	191	259	C5-3	141	210	B9-3	140	181
D1-4	180	228	C5-4	139	232	B9-4	143	171
D1-5	169	234	C5-5	144	202	B9-5	106	125
D1-6	176	245	C5-6	195	257	B9-6	138	193
D1-7	168	221	C5-7	180	238	B9-7	135	186
D1-8	184	257	C5-8	145	224	B9-8	175	178
D1-9	174	234	C5-9	168	204	B9-9	103	181
D1-10	182	234	C5-10	145	210	B9-10	148	185

TABLE IV.—*Time of setting.*

Sample No.	Initial set.	Final set.	Sample No.	Initial set.	Final set.
	h. m.	*h. m.*		*h. m.*	*h. m.*
B9-1	1 00	2 00	B9-6	23	2 30
B9-2	1 30	2 30	B9-7	50	1 35
B9-3	50	2 10	B9-8		
B9-4	48	1 33	B9-9	48	1 27
B9-5	35	1 10	B9-10	31	1 38

The above results led us to investigate more specifically the effect of air exposure on this class of cement. In Table V the depreciating effect upon the mortar of freely exposing a small amount of cement (about 400 grams) to the air in open jars for ten days is clearly shown. All mortar mixtures made from cement fresh from the sample package, dried or undried, and exposed to the air not longer than eighteen hours, did not set before the molding was completed and passed in tensile strength. All mortar mixtures made from cement exposed to the air for ten days, set before the molding was completed and therefore failed in tensile strength.

TABLE V.—*Test with dried and undried cement taken from paper bags.*

[Mortar, 1 to 3. Temperature of room during molding and setting, 29° to 30° C.]

Sample No. (same brand).	Condition.	Condition of mortar when molded.	Age.	Pounds per square inch.	Water used.
			Days.		*Per cent.*
F3-9	Dried and exposed to air 10 days	Set in 10 minutes	7	79	12.5
F3-9	Dried and exposed to air 10 days	Set in 12 minutes	7	98	14
F3-9	Dried and taken fresh from sample package.	Not set in 20 minutes.	7	186	14
F4-4	Dried and exposed to air 10 days	Set in 12 minutes	7	70	12.5
F4-4	Undried, fresh from sample package	Not set in 20 minutes	7	182	12.5
F4-4	Fresh from sample heated at 100° C., exposed 1 day.	Not set in 20 minutes	6	157	12.5
F4-4	Fresh from package undried	Not set in 20 minutes	7	([a])	12.5
F4-8	Dried and exposed to air 10 days	Set in 10 minutes	7	92	12.5
F4-8	Dried and exposed to air 10 days	Set in 12 minutes	7	101	14
F4-9 F4-10	Undried, fresh from sample package	Not set in 20 minutes	7	166 178	---------- 12.5

[a] *8 briquettes*—146 lowest 183 highest.

Percentage of water evaporated from F4-4 in drying was 0.66.

In all cases not specified the highest of four good breaks is recorded.

These results demonstrate that heating did not cause quick setting, and low tensile strength, but exposure to air in open jars for ten days did.

Table Va illustrates the same action:

TABLE Va.

[28 days; mortar, 1 to 3.]

Sample No.	Water.	Stored.	After 10 days.	After 30 days.	After 50 days.
	Per ct.				
X1	12⅛	Covered can	315	302	295
X1	12⅛	Uncovered can	247	205	158
X2	12⅛	Covered can	300	[a]298	202
X2	12⅛	Uncovered can	245	198	147

[a] Cover removed from can on thirtieth day.

The samples included in the next table were received at the laboratory in paper sacks on the 27th of the month. The next morning the two sacks comprising each sample were screened and well mixed. One half of each sample was then put into a tightly covered, galvanized-iron can, and the other half put back into the original bag. The time of setting was taken after seven, eleven, and twenty-four days with the results given in Table VI.

TABLE VI.—*Comparison of results of samples in paper bags and in closed cans.*[a]

Time gauged.	Worked after 7 days.					Temperature during—	
	Sample No.	Stored in—	Water.	Initial set.	Condition of paste.	Gauging.	Setting.
A. M.			*Per ct.*	*h. m.*		°*C.*	°*C.*
8.10	1	Can	21	1 10	Plastic	27	27 -29.5
8.20	2	Bag	21	60	do	27	27 -29.5
8.30	3	Can	21	1 22	do	27	27 -29.5
8.40	4	Bag	21	35	do	27.5	27.5-29.5
8.50	5	Can	21	60	do	27.5	27.5-29.5
9.00	6	Bag	21	12	do	27.5	27.5-29.5
9.10	7	Can	21	1 10	do	27.5	27.5-29.5
9.20	8	Bag	21	20	do	28	28 -29.5
9.30	9	Can	21	55	do	28	28 -29.5
9.40	10	Bag	21	13	do	28	28 -29.5
	Sample No. 8, worked after 11 days.						
8.25	8	Can	21	1 10	Plastic	27.5	27.5-30
8.35	8	Bag	21	17	do	27.5	27.5-30
8.45	8	Can	22	1 25	do	27.5	27.5-30
9.00	8	Bag	22	20	do	27.5	27.5-30
9.10	8	Can	24	1 30	Too plastic to hold its shape.	27.5	27.5-30
9.20	8	Bag	24	38		27.5	27.5-30
	Worked after 24 days.						
8.30	2	Bag	22	21	Very plastic	28	28 -30
8.40	3	Can	22	2 30	do	28	28 -30
8.55	3	Bag	22	20	do	28	28 -30
9.05	4	Bag	22	1 30	do	28	28 -30
9.15	4	Can	22	2 30	do	28	28 -30
9.25	8	Can	22	1 30	do	28	28 -30
9.35	8	Bag	22	23	do	28	28 -30

[a] All pats were made by the same operator by the Gillmore needle method described below. Before weighing, the original samples were thoroughly mixed.

Chemical analysis of number 8 sampled on the eleventh day gave:

TABLE VII.—*Analysis on eleventh day.*

Constituent.	From bag.	From can.
	Per cent.	*Per cent.*
Silica	19.80	20.24
Alumina	8.33	8.50
Iron oxide	2.75	2.98
Calcium oxide	63.44	63.32
Magnesium oxide	2.25	2.15
Moisture (110°)	0.32	0.14
Loss on ignition	3.14	2.52
Sulphuric acid (SO_3)	0.43	0.42

TABLE VIII.—*Moisture, loss on ignition and carbonic acid.*

Sample No. 8.	On twenty-fourth day cement from—		Difference.
	Can.	Bag.	
	Per cent.	*Per cent.*	*Per cent.*
Moisture at 110°	0.14	0.40	0.26
Loss on ignition after drying	2.63	3.92	1.29
Carbonic acid (CO_2)	1.14	1.64	0.50
Combined water	1.49	2.28	0.79

The rapidity with which this absorption of carbon dioxide and water may take place (the local climatic conditions being those of the early dry season) is shown in Table IX.

Two different brands were investigated, and in each case 50 grams of cement were taken from each of the samples specified, and put into 100 cubic centimeter beakers. These were accurately weighed and the free moisture then thoroughly driven off by four hours' heating at 130° C. The beakers were then allowed to stand in the balance room, open to the air, but protected from dust by paper coverings. The gain in weight was noted at the intervals of time designated. At the end of twenty-eight and one-half days, the moisture was again driven off by continued heating at 130° C. and the amount of water absorbed subtracted from the total absorption. The samples were again reheated after thirty-five days' additional exposure. The results obtained in detail are as follows:

TABLE IX.—*Changes in weight on exposure to air.*

Brand No.	Sample No.	Loss when received on heating at 130° C. moisture.	Gain in weight on exposure to air—carbon dioxide moisture, and water of hydration.														Lost on heating at 130° C.=moisture.	Total absorption other than moisture.	Gain in weight for 35 days, after second heating.	Lost on heating at 130° C. after 35 days moisture.	Total absorption other than moisture for 63½ days from the beginning.
			Hours.							Days.											
			18.	18.	6.	18.	24.	24.	48.	1.	1.	1.	1.	5.	7.	6.					
		P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct*	*P. ct.*	*P. ct.*	*P. ct.*
1	F6-1[a]	0.74	0.19	0.15	0.07	0.15	0.19	0.17	0.30	0.13	0.9	0.11	0.10	0.45	0.44	0.32	1.07	1.77	1.67	0.78	2.01
1	F6-3[a]	0.64	0.18	0.12	0.02	0.14	0.16	0.15	0.29	0.11	0.9	0.10	0.10	0.44	0.45	0.32	1.10	1.62	1.11	0.78	1.95
1	F6-5[a]	0.77	0.15	0.12	0.04	0.18	0.19	0.16	0.32	0.13	0.9	0.11	0.11	0.47	0.45	0.34	1.00	1.95	1.15	0.68	2.42
1	F6-7[a]	0.71	0.14	0.11	0.05	0.15	0.17	0.17	0.30	0.13	0.8	0.10	0.10	0.40	0.43	0.31	1.01	1.74	1.25	0.80	2.19
1	F6-9[a]	0.74	0.15	0.11	0.04	0.16	0.17	0.17	0.30	0.11	0.10	0.10	0.10	0.43	0.43	0.30	0.96	1.76	1.28	0.77	2.24
2	L208[b]	0.36	0.12	0.06	0.02	0.13	0.17	0.14	0.28	0.12	0.10	0.11	0.11	0.46	0.49	0.39	0.84	1.97	1.02	0.59	2.40
2	L213[b]	0.42	0.10	0.06	0.03	0.15	0.17	0.14	0.29	0.12	0.11	0.11	0.11	0.48	0.49	0.37	0.81	2.00	1.15	0.67	2.48
2	L217[b]	0.47	0.10	0.08	0.03	0.14	0.17	0.11	0.31	0.12	0.10	0.11	0.11	0.47	0.49	0.35	0.83	1.91	1.01	0.63	2.89

[a] Received in bag.

[b] Received in can.

TABLE X.—*After exposure for sixty-five and one-half days.*

Sample No.	Loss on ignition.	Carbonic acid (CO_2).
	Per cent.	*Per cent.*
F6-1	4.67	2.40
L208	4.25	2.42

The rapidity with which this action will progress depends upon climatic conditions, upon the nature of the cement itself and upon the ratio between the volume of the cement and the surface exposed. The action may take place very rapidly on the exposed surfaces, and yet penetrate into the mass very slowly.

A well-mixed cement was stored in a uncovered can for one month. Cement taken not lower than half an inch from the upper surface set in twenty minutes, while cement taken 6 inches below this surface did not set until two hours. It is therefore absolutely essential in order to secure uniform results from the same sample thoroughly to mix the cement before weighing; otherwise a wide discrepancy between the specific gravity, time of setting, and tensile strength may result which could not otherwise be accounted for.

The above data are considered sufficient to illustrate the effects of aëration, although in this laboratory we have many more experiments proving the same facts. It may be well to state that cements have been encountered which do not change to any appreciable extent after exposure for several weeks.

It has been shown (Table VI, can 8; eleven and twenty-four days) that cement, otherwise susceptible to a marked change by exposure to air, when preserved in closely covered galvanized-iron cans will be little affected by storage; and that thin paper bags do not eliminate the atmospheric influences. It has also been shown that the characteristics of a cement often undergo a change upon exposure which may be sufficient to make failures of otherwise acceptable tests. Therefore, it is evident that no system of cement testing, however accurate, will insure uniform or even comparative results until a proper, specified preservation of the samples after they are taken from stock is made compulsory.

As a result of the considerations given above, it would seem necessary so to modify the ordinary procedure that the quantity of the cement deemed necessary for the desired tests should be freely exposed to the atmosphere of the laboratory for seven days in a layer 1 inch deep, in order to determine the effects of aëration. A comparison of the specific gravity, setting time, and loss on ignition of the cement before and after exposure, will give valuable indications as to its nature. The determinations made before exposure will be consistent with the quality of the cement at the time the stock was sampled, and the second treatment will show the qualities liable to be developed by subsequent storage. If the

effect of exposure is considerable, troublesome variability of the brand may be readily attributed to this cause and the manufacturer will then know how to improve his product accordingly.

Changes caused by the atmosphere penetrate very slowly into the mass of the cement in barrels, because the wooden staves and heads keep the air from the product to a considerable extent and the mass of material is large, therefore, alterations which may develop very rapidly in a small sample exposed in the laboratory would not take place in the barrel until a much longer period of time had elapsed. Spalding[12] states that "the effect upon cement of retaining it a long time before using depends upon the nature of the cement and the method of keeping it. When the cement is inclosed so as to prevent the access of air, as in barrels, it may usually be preserved for a considerable time without experiencing any alteration, provided it is kept dry."

The fact that cements stored in good barrels undergo very little change by a month's seasoning is illustrated by the original and the re-test of the following cement, the results of which are recorded in Table XI. The samples for the re-test were taken a month after the original ones. All the samples were protected from aëration before testing, and the re-test gave only slightly lower results, although subsequent experiments showed that the cement rapidly deteriorated in time of setting and tensile strength when subjected to air exposure.

TABLE XI.[a]—*Original and re-test (one month later) of cement stored in barrels.*

ORIGINAL TEST.

Sample No.	Fineness.	Sp. gr.	Initial set.	Final set.	Tensile strength, neat.			Tensile strength, 1:3 mortar.	
					1 day.	7 days.	28 days.	7 days.	28 days.
			h. m.	*h. m.*					
1	95.8	3.07	2 10	5 00	392	516	640	240	285
2	96.5	3.07	2 15	5 10	351	563	605	200	278
3	96.2	3.08	2 10	5 00	354	532	687	221	300
4	96.0	3.08	2 10	5 00	351	558	610	232	296
5	97.0	3.08	2 00	5 00	312	542	653	222	300
Average	96.3	3.08	2 9	5 2	352	542	639	223	292

RE-TEST ONE MONTH LATER.

1	94.5	3.08	2 25	4 20	322	570	594	210	283
2	94.0	3.08	2 20	4 15	349	566	621	195	278
3	95.0	3.08	2 20	4 40	312	531	583	200	300
4	94.7	3.08	2 10	4 35	325	559	612	199	281
Average	94.5	3.08	2 19	4 28	327	556	602	201	285

[a] The soundness of all samples was satisfactory.

[12] *Ibid.*, 67.

Many engineers maintain with good judgment that a cement should not develop dangerous properties on exposure to the air and if it does so it merits rejection, especially if the unexposed samples show irregularity, since it is only practicable to test one barrel out of every ten or twenty in stock. It is also true that barrels often become broken in shipment, and should the cement which is so received develop dangerous properties, the strength of a whole structure might be weakened by its use.

Portions of the original samples of the cement the tests of which are recorded by diagrams numbers 1 and 2 were preserved and the tests after aëration in paper bags are shown in Table XII. All of these tests were manipulated in the same laboratory, and they show that this cement is more or less readily subject to the influence of aëration.

TABLE XII.—*Test of cement shown in diagrams numbers 1 and 2, after aëration in paper bags.*

Sample No.	Initial set, in minutes, after storage in paper bags for the times given.			Range of temperature during setting.	Specific gravity after—		
					Storage in bags.		Heating to red heat, 23 weeks' exposure.
	1 day.[a]	34 days.[a]	23 weeks.[b]		34 days.	23 weeks.	
				°C.			
X1	220	140	45	27–30	----------	3.02	3.14
X2	130	110	65	27–30	3.06	3.03	
X4	120	85	30	27–30	3.02	3.02	3.14

[a] 21 per cent water. [b] 22 per cent water.

THE DISPOSAL OF CAKED CEMENT.

It is usually specified that cement shall be screened through a 20-mesh sieve and thoroughly mixed before testing. The object of the sieving is to break up lumps and remove wood splinters, stones and other foreign substances. Such a procedure is of course proper. However, under certain conditions, the disposal of caked cement when it is present in considerable quantity should be more fully described.

Cement literature has repeatedly pointed out that the tensile strength of a caked cement is considerably below that of the original material before it formed lumps. This is due to the absorption of moisture and the subsequent partial setting. The difference that may result from such a change is illustrated in Table XIII, which gives the tensile strength developed by two samples of the same cement, one free from lumps and the other caked.

TABLE XIII.[13]

Condition.	Mixture.	7-day.	28-day.	3 months.	1 year.	2 years.	3 years.
All lumps	Neat	417	589	690	705	739	719
No lumps		686	756	798	858	857	805
All lumps	Mortar	131	244	326	373	372	373
No lumps		192	330	380	430	449	450

The disposal of these lumps then, especially those which are too hard to be broken up in the process of sieving, may exert considerable influence in the tensile strength obtained. If one tester pulverizes the hard lumps and mixes this powder with the original sample, and the other simply throws them away, uniform results can not be expected.

Should the cake be present in sufficient quantity to affect the tensile strength appreciably, the person requesting the tests should be notified of this condition. The presence of the cake may not be due to any fault or carelessness on the manufacturer's part. Improper storage while in the hands of the engineer or contractor may have caused it. Instances are also on record in this laboratory where caking was induced in the samples after they were taken from the stock. The samples were taken during a rain storm and through carelessness and incompetency on the part of the one handling them, they were allowed to get wet.

If specifications are to guarantee uniform and just results in all cases, the treatment of caked cement must be more fully described than it has heretofore.

INFLUENCE OF TEMPERATURE ON TIME OF SETTING.

The general rule for all cements is that increase of temperature increases the rate of setting. However, there is no fixed ratio between the temperature increase and the accelerated setting produced by it. The published reports of skilled operators vary in this respect, and L. Tetmaier,[14] after years of the most careful work was forced to admit that "different cements are differently influenced by alteration of temperature * * * and it is scarcely possible to deduce a general law for even one class of cements."

The results we have obtained on the setting time of various cements, worked in the cold-storage room and at local temperature, have shown that the samples, in this respect, could be divided into three classes:

1. Slow setting cements, little affected by a variation of temperature from 20° to 30° C.

[13] Griesenauer, *Eng. News* (1906), **55**, 68.
[14] *Soc. Chem. Industry* (1893), **12**, 1036.

2. Cements which are slow setting at 20° C. but quick setting at 30° C.
3. Cements which are quick setting at 20° C. and also at 30° C.

As these results were obtained while we were endeavoring to determine the variation which this climate might cause in tests which according to American standard specifications are at about 20° C., we will publish them in full in Tables XIV, XV, XVI, and XVII.

In all the following determinations the cement was sieved and then very thoroughly mixed. To eliminate any effect of unequal atmospheric exposure each sample of 500 grams was put into a dry, clean bottle and tightly corked until used. In gauging, the water was allowed to soak in for one minute, and then the paste was vigorously troweled for four additional minutes.

TABLE XIV.—*Class No. 1, slow-setting cements, little affected by variations of temperature.*

Bottle No.	Temperature when made.			Temperature of room during setting.	Water.	Initial set.	Final set.	Condition of paste.
	Cement.	Water.	Room.					
	°C.	°C.	°C.	°C.	Per cent.	h. m.	h. m.	
1	19	19	19	19 -19.5	20.66	2 35	6 15	Slightly plastic.
2	19	19	19	19 -19.5	21.66	2 45	6 15	Plastic.
3	19	19	19.5	19 -19.5	22.66	3 00	6 20	Do.
4	19	19	19.5	19 -19.5	23.66	3 00	6 20	Very plastic.
5	32	32	31	32 -32.5	20.66	2 35	6 20	Plastic.
6	28	28	28.5	28.5-31	21.66	2 20	4 20	Do.
7	28	28	28.5	28.5-31	22.66	2 20	4 30	Do.
8	28.5	28.5	28.5	28.5-31	23.66	2 55	5 35	Very plastic.
9	29	29	30	30 -31	23.66	2 25	4 15	Do.

TABLE XV.—*Class No. 2, slow-setting cements at 20°, quick-setting at 30° C.*

Bottle No.	Temperature when made.			Temperature of room during setting.	Water.	Initial set.	Final set.	Condition of paste.
	Cement.	Water.	Room.					
	°C.	°C.	°C.	°C.	Per cent.	h. m.	h. m.	
1	31	31	31	31 -33	21	([a])	([a])	
2	31	31	31	31 -33	22	25	2 30	Slightly plastic.
3	28	28	28.5	28.5-30	21.66	21	2 50	Do.
4	28	28	28.5	28.5-30	22.66	28	3 00	Plastic.
5	28.5	28.5	29	29 -30	23.66	32	3 10	Very plastic.
6	19.5	19.5	19.5	19.5-20.5	21.66	2 32	3 40	Slightly plastic.
7	19.5	19.5	19.5	19.5-20.5	22.66	3 30	4 40	Plastic.
8	19.5	19.5	19.5	19.5-20.5	23.66	3 50	5 00	Very plastic.

[a] Impossible to make pat.

To determine the effect of gauging in the cold-storage room and setting in the laboratory, and vice versa, two pats were made from each paste and one subjected to the change in temperature; the results are recorded in Table XVI.

TABLE XVI.

Bottle No.	Pat No.	Temperature when made.			Temperature of room during setting.	Water.	Initial set.	Final set.	Condition of paste.
		Cement.	Water.	Room.					
		°C.	°C.	°C.	°C.	Per cent.	h. m.	h. m.	
1	1	20.5	20.5	21.5	20.5-22	22.66	2 15	--------	Plastic.
	2	20.5	20.5	21.5	32 -32	22.66	55	2 10	Do.
2	1	20.5	20.5	21.5	20.5-22	22.66	2 20	--------	Do.
	2	20.5	20.5	21.5	32 -31.5	22.66	60	2 30	Do.
3	1	32	20	32	32 -31.5	22.66	26	1 55	Do.
	2	32	20	32	20.5-22	22.66	50	--------	Do.
4	1	32	32	32	32 -31.5	22.66	21	1 21	Do.
	2	32	32	32	21.0-22.0	22.66	38	--------	Do.

TABLE XVII.—*Class III, cements which are quick setting at 20° and also at 30°.*[15]

Bottle No.	Cement.	Temperature of water, cement, and room.	Temperature of room during setting.	Water.	Initial set.	Condition of paste.
		°C.	°C.	Per cent.	h. m.	
1 and 9	A	17-18	17.5-18	22	1 40	Plastic.
2 and 10	A	29-30	29 -30.5	22	1 20	Do.
3 and 11	A	17-18	17.5-18	21	1 25	Do.
4 and 12	A	29-30	29 -30.5	21	1 20	Do.
5 and 13	A	17-18	17.5-18	20	40	Slightly plastic.
6 and 14	A	29-30	29 -30.5	20	45	Plastic.
7 and 15	A	17-18	----------	19	([a])	([a])
8 and 16	A	29-30	----------	19	([a])	([a])
1 and 3	B	17-18	17 -18.5	24	28	Very plastic.
2 and 4	B	29-30	29 -31	24	24	Do.

[a]Impossible to make pat.

Remark.—Pastes made with 20 per cent of water were more plastic when made at 30° than at 17°.

MOIST-AIR CLOSET.

Another possible source of error which may be accountable for considerable variation may develop during the moist-air treatment.

Most specifications allow the briquettes to be stored for the first twenty-four hours in a moist-air closet or under a damp cloth. Moist-air closets are given the preference, as unequal drying often occurs in using the damp cloth. A well-constructed moist-air closet is essential to uniform results.

One condition in the use of a moist-air closet that is liable to have considerable influence upon the result of the cement tests should be taken

[15] This table also shows the marked effect that 1 per cent of water more or less, will produce upon the plasticity and time of setting of some cements.

into consideration. This is produced by the heating of the cement after it is gauged and molded. Many cements heat considerably at some period of the stage of early setting and hardening, the rise in temperature often being as much as 10°C.; it may take place in five minutes, or it may not occur until many hours after the gauging.

C. Prussing[16] states that "many slow setting cements of excellent quality begin to set after five or six hours and then set completely in one hour, giving a rise of temperature of 5° to 7°C." The heat generated by briquettes placed under a damp cloth is not confined, as it is readily conducted away into the surrounding atmosphere. Moist-air closets are constructed to insulate the interior from outside heat influences as much as possible, and as a result the heat generated by the briquettes is confined; so that in a cubical moist-air closet of 2 feet on the side which was used to store briquettes after they were removed from the molds, the temperature often rose to 40° (30° being room temperature) when it held from 80 to 100 briquettes. A number of slow-setting briquettes made at different, successive intervals of time, or worse still a mixture of quick, normal, and slow-setting cements, will under these conditions not be subjected to the same uniform temperature, or to a temperature change that is characteristic of it during its most critical setting and hardening period; and the same is true of the storage of pats made for the time of setting when many are placed in one compartment after gauging.

It is well known that the temperature conditions under which cement sets and hardens will influence its tensile strength. Therefore, the practice of storing numerous briquettes in one compartment of a moist-air closet is very liable to cause abnormal one, seven and twenty-eight day breaks of some of them. Pats for time of setting similarly stored may be also affected to such a degree that an otherwise slow-setting cement may become quick setting.

We suggest two ways of overcoming this objectional feature of the ordinary closet. The heat generated by the setting cements may be conducted away by means of a forced ventilation of air saturated with moisture; or only briquettes and setting pats of the same cement made at practically the same time should be placed in a small, insulated compartment. The former method will maintain the interior of the compartment at nearly the same temperature as that of the laboratory, while the latter will meet the conditions of actual service, as the heat generated by the cement is not readily conducted away. Laboratory tests should coincide as closely as is possible with the actual conditions of construction work, where large volumes of concrete are tamped into wooden frames. The heat generated in such a large mass (especially in the center of it) is not conducted away by ventilation and it is in fact partly insulated

[16] *Thonind. Zeit.* (1894), **18**, 251.

by the wooden molds. Therefore, a moist-air closet formed of several small, insulated compartments, each with its own pan of water, is best adapted for the purpose. Such a moist-air closet has been constructed for this laboratory.

Standard cement specifications should include a definite form of moist-air closet with a complete description of the materials for its construction, its dimensions, and directions for its use; otherwise one source of the so-called personal error will persist.

TIME OF SETTING.

The American Society has adopted the Vicat needle method for determinations of the time of setting. It seems to be the general impression that the Gillmore method does not insure the desired accuracy, and many cement testers will regret that such a convenient and time-saving process has been supplanted by a more cumbersome one; still the Gillmore method, if properly regulated, can be made accurate, reliable, and impartial and at the same time retain its simplicity, even though the meager directions in the United States Army specifications do not insure uniform results between different operators and at times imposes unjust tests upon some good cements.

Merz, Meyer, Schiffner, Bohme and many others have each pointed out that to determine the time of setting of a cement it should be gauged with a quantity of water proper to it.[17] It has often been demonstrated in this laboratory that 20 per cent of water is not enough to meet the requirements of the fineness, specific gravity, chemical composition, and physical properties of many good Portland cements sufficiently to produce a paste plastic enough to be molded into a pat. The resulting paste is often so dry and non-cohesive that it will not stick together or to the glass plate; and yet 1 to 3 per cent of water in addition will produce the desired plasticity and cohesiveness.

The whole phenomenon of the manufacture of artificial stone from finely powdered cement is one of solution, hydration and subsequent crystallization. The addition of sufficient water is essential for proper solution and hydration. The addition of too much water is to be avoided because of its effect upon the subsequent crystallization, and because the density of the paste must allow of proper manipulation. Therefore, it is very evident that plasticity and not a given percentage of water should be the condition regulating the paste for cement pats.

The insistence of the United States Army engineers upon a paste gauged with 20 per cent of water seems to be a striking illustration of Spalding's assertion that[18] "tests may be imposed which in nearly all

[17] *Soc. Chem. Industry* (1891), **10**, 928.
[18] *Ibid.*, 87.

cases will secure good material, but often at the expense of rejecting equally good or better material."

Merz, Meyer, Schiffner, and others also insist that even when cement is gauged to the proper plasticity there is a large personal error due to the operator himself. After a careful study of this personal error, we have come to the conclusion that it is mainly due to the following five causes:

1. The manner of applying the needles.
2. The presence of small air bubbles near the surface of the pat.
3. The difference in the amount of water brought to the surface in patting the cement together and its presence there in a more or less liquid layer.
4. The difficulty in judging the exact time when the needles cease to make a "visible impression."
5. The difference in plasticity.

To overcome the first difficulty the pat should be made with a flat (not rounded as specified) top as illustrated in fig. 1. The needle should then be applied very gently and after the flat point rests upon the surface of the pat the full weight of the needle should gradually be applied. Failure to hold the needles in an exactly vertical position will often cause the edges to indent where the flat point would not.

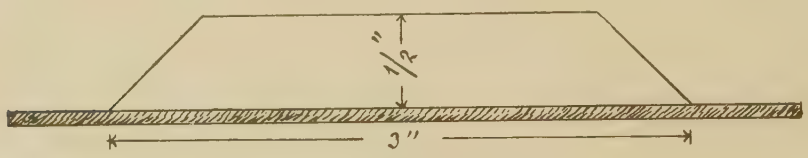


Fig. 1.

To overcome the second, third and fifth difficulties, the cement is gauged with the least amount of water which after one minute's soaking and four additional minutes of vigorous troweling will produce a paste sufficiently stiff to retain its shape, and yet so plastic that the initial needle will sink almost to the glass plate when applied directly after forming the pat. A ball of this paste when dropped from a height of 70 centimeters will flatten very slightly and will not crack. A lump dropped from the point of the trowel will leave the surface of the latter comparatively clean. In forming the pat the cement should be thoroughly patted together with the flat of the trowel. This eliminates the air bubbles near the surface and also brings the excess of water to it. In forming the flat top, the hyperaqueous cement should be wiped off as much as possible with the edge of the trowel, and the surface left smooth and firm.

Difficulty number five is especially marked in slow-setting cements, as sometimes a slight indentation will persist for hours and in the judgment of an individual operator, may even not be fixed within thirty to

sixty minutes. However, this uncertainty can be greatly overcome if the needle is carefully applied at intervals of five, ten, fifteen, or twenty minutes according to the rapidity of set, indentations being made in a row. After the pat has become dry, the point where the needle ceases to penetrate is easily recognized (especially so if the surface is slightly moistened), and the time can then be calculated according to the number of previous indentations.

Figs. 2 and 3 illustrate a quick and a normal setting cement, worked according to these directions.

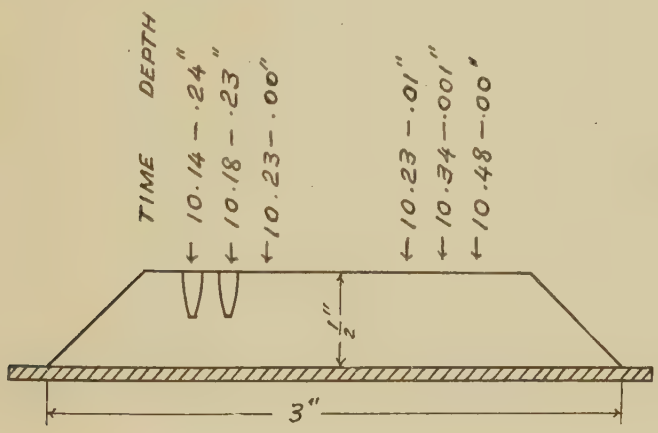


Fig. 2.

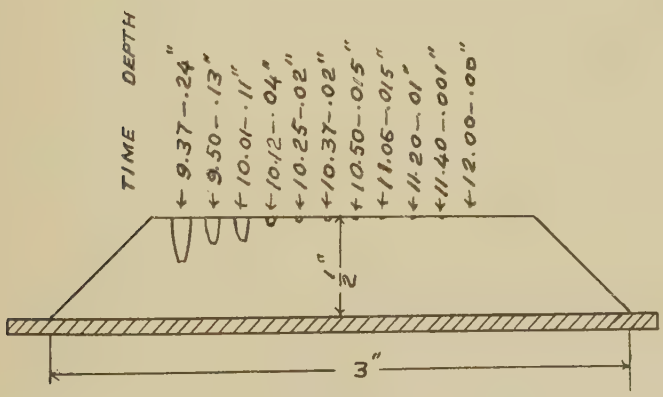


Fig. 3.

This method, once the details are mastered, is just as convenient and quick as a less accurate one. For research work and for cements the setting qualities of which are close to the requirements of specifications, it is especially valuable, as we have found that two pats of the same paste will compare almost exactly, and that even different operators will not vary 10 per cent if they are careful and efficient.

However, it has been our experience that, as Spalding[19] states, "the rate of setting of neat paste gives but little indicaton of what the action may be with sand." Several instances of satisfactory neat and unsatisfactory mortar tensile strength have been encountered in this laboratory, because of the more rapid setting of the cement when combined with sand. It is deemed sufficient to state here that the mortar and neat set must vary because of the differing percentage of water which is used, the difference in physical manipulation, in the air exposure, in mixing, the physical and possibly also the chemical influence of the sand.

For the thorough study of the nature of some cements the determination of neat and mortar setting qualities may be essential. A simple method to determine the setting time of a mortar is here suggested. The beginning of setting when sufficiently rapid appreciably to influence the briquette manipulation is characterized by sudden drying and a slight stiffening of the mortar. If a mixture is made as if for briquettes and the mortar then placed on a glass plate and divided into cubes with the trowel, a slight set may readily be detected when a cube, upon being crushed between the finger and thumb, feels dry, crumbles apart and offers a slight resistance to the crushing force. A harder set may be arbitrarily fixed and determined when the setting has progressed to the extent that a one inch cube dropped from a height of one foot will not crack.

However skilled the operator may be, or however accurate his method, uniform results even by the same operator and on the same cement can not be insured unless the precautions described under the previous headings of "Effects of aëration" and "The moist-air closet" are heeded. Thus, the first sample taken from near the surface of an exposed package not previously mixed, may set in twenty minutes, while succeeding samples taken at a lower depth may not set for hours. When it is desired to make a series of comparative setting tests on the same cement it is advisable to remix the sample thoroughly before weighing and then store the cement in tightly stoppered, wide-mouthed bottles until it is used. The pats should be stored in insulated compartments of the moist-air closet to avoid the influence of the heat liable to be generated by other pats during setting.

SOUNDNESS.

Tests for soundness, like setting pats, should be made with a paste of the correct plasticity. If too little water is used in gauging, the cement will not adhere properly to the plate, and lack of cohesion in the cement itself may result in cracks not due to its subsequent expansion or contraction. If too much water is used, shrinkage cracks of such a nature as to be easily mistaken for evidence of unsoundness, may occur.

[19] *Ibid.*, 111.

This laboratory uses the same plasticity in its tests for soundness as for setting pats. The cement in this condition is thoroughly wet and pliable, but still stiff enough to retain its shape, therefore it meets all the requirements of a just test. Uniformity between different testers is also secured, because 1 per cent of water more or less would so change the nature of the paste that it would be rendered either too dry or too liquid. The results obtained depend much upon the skill of the operator. Sudden changes in temperature during the steaming and boiling tests should always be avoided. Moistening the surface of the glass plate with a damp cloth before applying the paste will insure better adhesion to the plate. A ball of the paste should then be applied to this surface and patted down very vigorously into the desired shape. Vigorous patting with the flat of the trowel eliminates any interior cracks, reduces the air bubbles to a minimum and brings the excess water to the surface. For soundness, the top of the pat should be arched and the rim troweled to a thin edge as shown in fig. 4. Pats made in this manner will not warp or crack unless the cement is faulty.

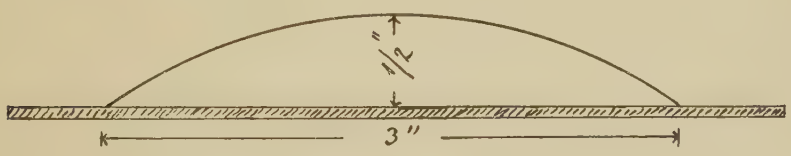


Fig. 4.

We have noticed that different testers interpret the results of soundness tests in different ways. Some operators will report as "unsound" a cement that shows the least trace of warping even after air exposure. Cements showing only slight incipient disintegration are often reported as "disintegrated." In like manner "off plate" and "cracked plate" are often attributed to expansion and contraction. Such an interpretation is unjust to the manufacturer, as warping and cracking to some extent under certain conditions are not to be considered dangerous. A sound pat combined with a broken plate does not necessarily indicate dangerous contraction or expansion. Every cement expands more or less, and in this case the adhesion between the cement and the glass is very strong. As the glass also has an expansion factor, all such cases should be reported as satisfactory if the pat itself shows no sign of cracking or warping. To insure a perfect understanding between the manufacturer, engineer and tester and to avoid unjust or misinterpreted results, specifications should include a descriptive chart of the proper standard interpretation by which the extent, significance, and importance of the various degrees of warping, cracking, disintegrating and shrinking are to be regulated. This labora-

tory has adopted the standard portrayed and described by Taylor and Thompson [20] in order to insure a complete comprehension in this respect.

Much diversity of opinion exists regarding the rejection of a cement which fails to meet the boiling test,[21] but we regard such a cement as dangerous if it is to be used in works exposed to the heat of the tropical sun.

Excess of lime, coarseness of grinding, insufficient seasoning, and underburning of a cement may cause it to fail to pass the soundness test. If lime is the cause, storage may eliminate the defect, as the free lime would thus be changed to the carbonate, or slaked, and so would not cause subsequent expansion.

Many engineers believe that failure to pass the hot test is not a proof of inferiority, as the cement so failing, if mixed with sand or some other aggregate, has produced durable masonry; it is also a known fact that thoroughly slaked lime paste can be added to a Portland cement mortar without injurious results. We suggest that, as is the case in determining the time of setting, some specification be devised to test the mortar mixture as well as the neat paste.

TENSILE STRENGTH.

The variation in the breaking strength of both neat and sand briquettes is a source of trouble to every cement tester, and despite every effort to eliminate this error, breaks continue to be variable with a persistence that makes it necessary to double or treble the number of briquettes otherwise required. We have made a thorough study of this variation and as a result have come to the conclusion that only a portion of it is due to the personal error of the operator, and that the remainder is caused by the characteristics of the cement itself.

Personal error even with the most careful manipulation, may be produced by (1) unavoidable variation in troweling; (2) difference in the force of the blows; (3) lack of equality in forming each layer of the briquette; (4) variation in the size and shape of the mold; (5) difference in the size and shape of the sand particles; (6) personal error in machine operation; (7) unavoidable internal strains and voids caused by the manipulation which the specifications impose (8) the impossibility of securing a perfectly homogeneous mixture; (9) variation in drying.

The errors caused by the natural characteristics of the cement, and which need more extended explanation, are as follows:

1. It is obvious that it is impossible to expose the same number of cement particles to the action of the air for the same length of time in

[20] Concrete, Plain and Reinforced. New York (1907), 103–107.

[21] *Loc. cit.*

each instance during troweling; those outside will be exposed more than the inner ones and the evaporation caused by contact with the air may cause setting. We would expect a greater variation from this cause in quick setting cements than in slow ones; and our experience has confirmed this. Slow setting cements give the least variation in tensile strength.

2. Another cause of variation is the tendency possessed by some cements to enclose air bubbles, thus producing irregular voids.

3. Unequal hardening of the exterior and the interior of the cement briquettes may cause differences in heat generated during setting and variable water action during submersion. This cause may also produce internal strains and voids. This variability would also be especially marked in quick setting cements.

4. Irregularity in the intermingling of the crystals during crystallization.

In summarizing the above conditions, only errors which are unavoidable and such as might occur in a batch of four briquettes made and manipulated in the same manner and under the same conditions have been assumed, and our endeavor has therefore been, if possible, to minimize the personal error, and to this end a new type of tamper differing from that specified by the United States Army engineers was adopted. We found it impossible to raise the specified tamper exactly one-half inch at every blow, and at the same time to apply the blow just where we wanted it. A simple, accurate, easily and quickly manipulated tamper which gives the same force to every blow, and hits the exact spot desired, was therefore devised by us.

A (fig. 5) is a thin, hollow cylinder open at *d* and closed at *e*. It weighs about 60 grams. *B* (fig. 7) is a solid brass rod which weighs just 1 pound. The end bearing the lug *b* is inserted into the cylinder *A*, *b* following the groove *a*. To manipulate this instrument, the rod *B* is held near the top with the thumb and forefinger of the right hand, *A* being held in the same way with the left. The lug *b* is drawn hard against the angle in the groove *a*, and the end *e* is placed on the surface of the cement just where it is desired to have the blow strike. The rod is then dropped and at the same time the hold on *A* is loosened. A little practice will enable any one to operate this tamper very quickly, and at the same time to deliver an unvarying blow due to the half-inch drop of the one pound rod. The blows can be directed at will and it is not possible to hit the edges of the mold.

The United States Army specifications direct the tester to raise the tamper one-half inch above the surface of the cement. As the paste and mortar are put into the molds in a lumpy condition, no plane surface line is presented, and as we wished to control the force of each blow as much as possible, a surfacer was devised to enable us to have uniform plane.

Fig. 6.

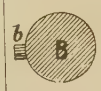


Fig. 8.

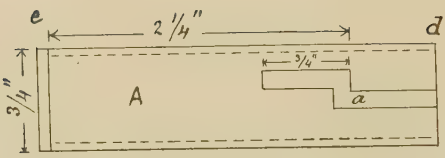


Fig. 5.

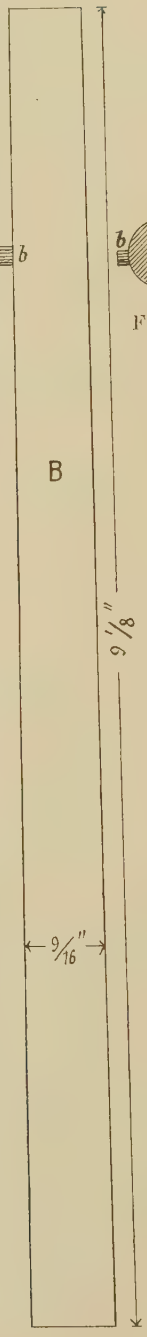


Fig. 7.

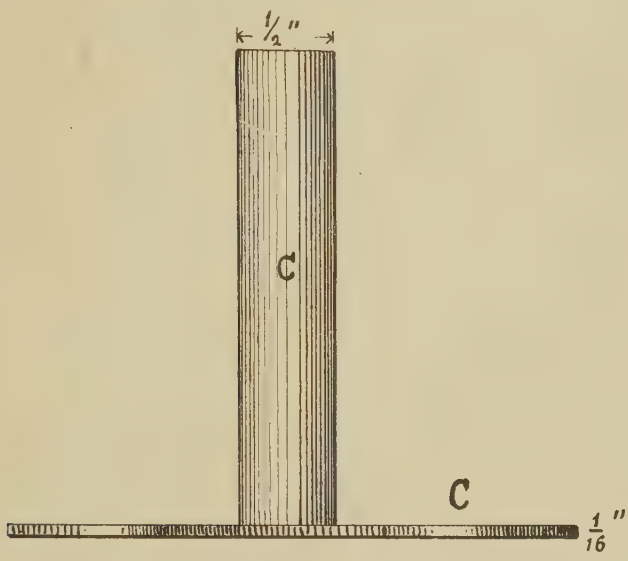


FIG. 9.

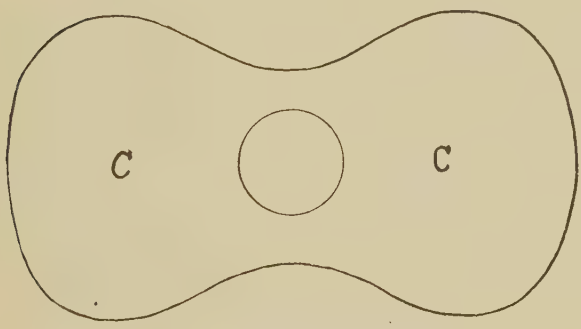


FIG. 10.

This surfacer is made of steel and of the form shown in figs. 9 and 10. The flat surface *c* fits loosely into the mold. The layer of cement is placed into the latter, distributed as evenly as possible with the fingers, and then lightly pressed together with the surfacer. Treating each layer in this manner also keeps the material from sliding and working around during tamping.

To secure uniform effects of tamping it is also essential that the successive layers of each briquette be made as nearly equal as possible. This is easily attained by the use of a small beaker as a measure. After selecting a beaker of the correct capacity it is scooped full of cement, the excess shaken off, and the remainder turned into the mold.

It is not advisable in mortar manipulation to use a measure; the mortar adheres to the glass to some extent and, in dumping, the sand readily falls out, but some cement paste remains attached to the beaker, thus changing the ratio of 1 to 3. We quickly form the mortar into a

flat square on the slab, and by pressure with the edge of the trowel rapidly divide it into sixteen cubes. One such cube forms each layer of the briquettes.

In tamping the last layer, it is advisable first to lay an empty mold exactly over the other. The empty mold acts as a guide for the tamper and so avoids the possibility of the loss of the full effect of a blow caused by striking the edge of the mold.

The United States Army specifications direct that each layer of cement in the molds be uniformly tamped with thirty blows. There is no possible way to avoid unequal overlapping of blows with the tamper specified (both round and square). As a result, and also because of the fact that the cement is put into the molds in a more or less lumpy condition, certain voids and excess in the consistency and compactness of the resulting briquettes are unavoidable. Air spaces also form with more or less irregularity. These produce internal strains and variation in cohesion, and consequently differences in the breaks. This illustrates one case of a specification which imposes variability of results upon the tester.

The American Society method eliminates the greater part of this trouble. The paste is more homogeneous and plastic (not lumpy); it is readily pressed into the molds by the fingers and a subsequent patting of the briquette with the flat side of the trowel will eliminate any variation in compactness caused by unequal pressure of the fingers.

The natural tendency in tamping briquettes is to strike the middle, narrow section more than the wider ones; it follows that the resulting briquette is denser in the middle portion. This is the main cause of bad breaks, besides giving a higher result than is just if uniformity of tamping is followed. It is just as essential not to weaken the middle section below the average density. Such a method of tamping will give good breaks, but lower the tensile strength.

After experimenting with many methods to secure as uniform tamping as possible, conducive to good breaks and greatest strength, we have adopted the following method which can be accurately carried out with our automatic tamper.

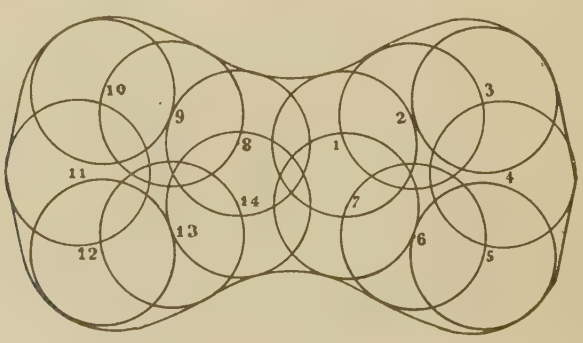


Fig. 11.

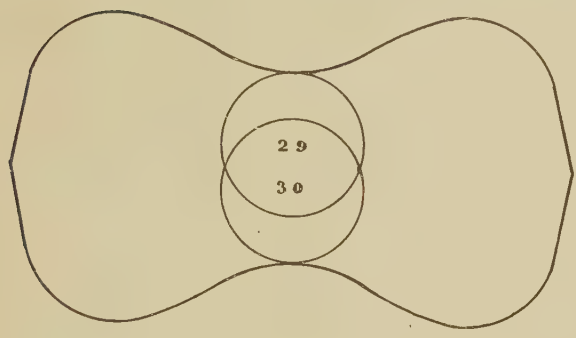


FIG. 12.

The fourteen blows illustrated by fig. 11 are repeated and the final two struck directly across the middle as shown by fig. 12.

Neat briquettes made in this way always break across the center in the Fairbanks roller clips, and seldom vary more than 10 per cent from the highest (5 per cent from the mean). At times, batch after batch will break within a few pounds. Again, at rarer intervals, an occasional break occurs which is 20 per cent or more away from the normal. This variation depends to a great extent upon the nature of the cement and the consistency which the per cent of water used produces. Quick-setting cements give the greatest variation in results.

Sand briquettes still continue to differ considerably, as is true with all other methods. The variation in the size and shape of the sand particles and the corresponding voids and excesses of cement are such that it does not seem possible to contrive any method to eliminate the differences in the tensile strength. The chief value of our system in this respect is that it insures good breaks and hence gives more data to report from. For the purposes of investigation and for work which is under dispute, the question of variation in the force of the blows and their application is eliminated by our method. It is also true that the mechanical tamper renders it possible to depend upon the labor of assistants. The variations in tamping having been eliminated, a smaller number of breaks will suffice. We find that four briquettes from two batches of mortar will almost invariably cover the entire range of possibilities, and show any undue variation in the quality of a series of cement samples, this is illustrated by Table XVIII which shows the uniformity of the cement very plainly, despite the small number of breaks.

TABLE XVIII.—*Showing the uniformity of breaks due to the method of tamping.*[a]

No.	Fineness, specific gravity, and set.[b]						Tensile strength in pounds per square inch.				
	Fineness (100 mesh).	Specific gravity.	Initial set.		Final set.		Neat cement.			1 cement to 3 sand.	
							1 day.	7 days.	28 days.	7 days.	28 days.
			h.	*m.*	*h.*	*m.*					
F2-1	95.9	3.06	1	10	2	15	345	558	625	166	250
F2-2	96.3	3.07	1	15	2	10	331	553	650	164	271
F2-3	96.6	3.07	1	30	2	25	327	495	582	162	274
F2-4	97.0	3.07	1	30	2	25	300	511	568	166	260
F2-5	96.8	3.07	1	30	2	30	322	520	585	159	249
F2-6	96.0	3.07	1	23	2	33	330	528	622	157	245
F2-7	97.0	3.06	1	35	2	45	351	534	562	163	247
F2-8	96.5	3.07	1	37	2	40	334	506	611	163	260
F2-9	96.5	3.06	1	25	2	45	335	503	620	158	249
F2-10	96.4	3.07	1	30	2	50	338	522	600	175	256
Number of briquettes broken							2	3	3	4	4

[a] See also Table XI.

[b] Soundness satisfactory at the end of six and twenty-eight days, respectively.

The following diagram demonstrates the value of our method: Twenty-eight briquettes of cement, ground extremely fine, were made and four briquettes were broken every other day. The results are plotted on the curve shown by diagram number 3.

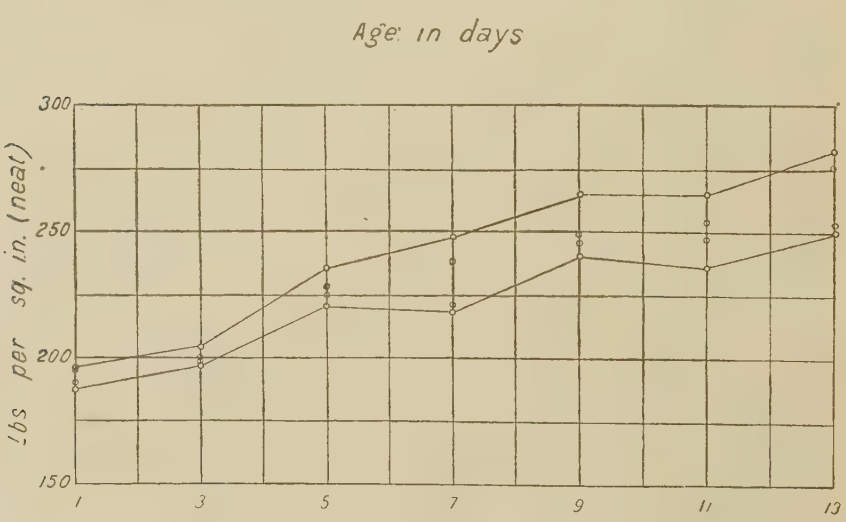


DIAGRAM No. 3.

This curve is of interest as it plainly demonstrates the unequal action of water upon the briquettes, the tendency being for the curves of the extreme breaks gradually to grow farther apart. The low tensile strength neat, as a characteristic of extremely fine grinding, is also of interest.

In this laboratory all sand briquettes are broken in a German machine (Hugershoff), invented by Michaelis. The Fairbank's roller grips are so heavy and the surface of contact so narrow that they crush through the majority of 7-day mortar briquettes, giving bad breaks and figures representing low tensile strength, and this is especially true of cement which does not in itself develop great strength. The German machine offers a wider surface of contact and the grips support their own weight. Comparative tests carried on for months in routine work give 10 per cent higher results with the latter, but the variation is greater, as the machine is more delicate; the probability of obtaining bad breaks is also greater, but when our system of tamping is used this probability is reduced to a minimum.

It is especially difficult in this climate to obtain uniformity in the demonstration of tensile strength. The laboratory temperature seldom falls below 26°, and is often as high as 31°.5. Our own experiments bear out the conclusions derived from all published data on the influence of temperature. High temperature is conducive to slightly greater tensile strength on 7- and 28-day tests, and also to a greater variation between breaks.

The different tensile strengths secured by different machines, molds, and grips is another reason why there is such a great lack of uniformity between different laboratories. Johnson, Sabin, Thompson and Taylor, Spalding, Butler, and in fact almost every authority on cement testing, devote considerable space to illustrating the variable results that occur from this source. A specification that allows any form of grip and mold can not hope to accomplish its purpose. The Army specifications allow the use of any tensile strength system. The American Society specifications recommend a special form of briquette and regulate certain important factors in the grips. To insist upon a certain machine, grip, and mold would be a rather delicate undertaking, but until this is done there may always be a large difference due to "personal equation" between the tensile strength determinations between different laboratories.

The American Society introduces a very good check upon the mixing and molding of briquettes by specifying that they should be weighed just before immersion and that all which vary more than 3 per cent from the average, should be rejected; in this way greater certainty in results is obtained. It is very easy to work within these limits, and every tester should strive to attain weights which approach each other within 1 per cent. This determination of weight, in addition to being a check upon the uniformity of mixing and molding, may also disclose the effect of unequal drying and of imperfect molds. Sand briquettes are more liable to variation beyond the limits of 2 per cent than are neat. This difference is due, as is the variation in breaking strength, to the lack of uniformity in the size and shape of the sand particles and the irregularity in voids.

The conclusion would naturally be drawn that the greater the density of the briquette, the greater would be its tensile strength. This is not true within limits of 2 per cent, as the other reasons for "personal error" above described may overcome the natural tendency to high tensile strength caused by the density of the material. In sand mixtures, also, a high density may simply show that more sand and less cement have been used.

These facts are illustrated in our routine work and shown by Tables XIX and XX.

TABLE XIX.—*Mortar briquettes, 1 to 3; 12½ per cent water; tamped.*

Sample No.	Time in days.	Tensile strength in pounds per square inch.	Weight in grams.	Sample No.	Time in days.	Tensile strength in pounds per square inch.	Weight in grams.
F1-5	7	171	131.0	F1-8	7	191	131.1
	7	184	129.9		7	177	130.7
	28	214	130.5		28	221	130.0
	28	200	126.5		28	233	129.2
F1-6	7	176	131.4	F1-9	7	188	131.1
	7	192	130.6		7	177	130.5
	28	188	131.0		28	244	131.0
	28	195	130.0		28	232	132.0
F1-7	7	178	128.7	F1-9	7	182	130.0
	7	191	129.3		7	192	130.3
	28	223	128.6		28	238	130.8
	28	216	127.9		28	235	131.0

TABLE XX.—*Neat briquettes made from sample Y1 according to American Society specifications.*

Age in days.	Tensile strength in rounds per square inch.	Weight in grams.	Average weight in grams.	Age in days.	Tensile strength in pounds per square inch.	Weight in grams.	Average weight in grams.
28	603	137.3	137.8	28	636	136.5	136.6
28	665	138.8		28	613	136.6	
28	(539)	138.2		28	599	136.5	
28	638	137.0		28	609	136.8	
28	(686)	137.5	137.9	28	621	137.2	137.0
28	636	137.8		28	(661)	137.7	
28	620	137.8		28	631	137.0	
28	625	138.6		28	617	136.4	

For some time this laboratory was forced to manipulate all cements strictly according to United States Army Engineer specifications, with 20 and 12.5 per cent of water for the neat and mortar tests, respectively. Twenty per cent of water will not satisfy the chemical and physical possibilities of many good Portland cements, and the following table illustrates this fact:

TABLE XXI.—*Variations in tensile strength with varying quantities of water; 7-day results.*

Sample No.	Neat.		1 to 3 mortar, 12.5 per cent water.
	20 per cent water.	22.5 per cent water.	
D4-2	219	633	213
D4-4	182	614	208
D4-6	167	612	216
D4-8	152	600	200
D4-10	178	603	209

The highest results of four good breaks are recorded in each instance.

It will be noticed that the sand briquettes (12.5 per cent water equal to 50 per cent calculated on the cement) present higher results than the neat with 20 per cent of water; and that 2.5 per cent additional for the paste increases its tensile strength over 200 per cent. The following table shows a failure in either case:

TABLE XXII.—*Varying quantities of water used with a failing cement.*

Sample No.	7 days neat.		28 days neat.	
	20 per cent water.	24 per cent water.	20 per cent water.	24 per cent water.
L181	200	404	274	468
L184	257	438	350	523
L186	262	418	318	451

Twenty-seven per cent of water gave lower results than 24 per cent.

It is a simple matter to judge when a cement contains enough water if the method of tamping is used. The surface must be wet when the last layer has been tamped into the mold and of not quite the plasticity described for the pats used in determining the time of setting. A dry surface is positive proof that very low tensile strength will result. The determination of the "normal consistency" can not be used for this purpose as the resulting paste is too slushy for tamping.

If 20 per cent of water gives too dry a mixture, we add an additional quantity sufficient to bring the water to the surface after tamping. The percentage of water necessary to accomplish this result is included with the report of the tests. The results obtained in this way by our tamper and method of tamping are satisfactory, consistent and true to the quality of the cement. The best result of four good breaks is sufficient for all routine work.

The United States Army specifications state that the best results are

obtained with a mortar containing 10 to 12.5 per cent of water, and suggest the use of 12.5 per cent. This is contrary to best practice and results. The correct amount of water for sand, as for neat briquettes, depends upon the nature of the cement, and the amount of water necessary to wet the surface of the sand. We find that 12.5 per cent is too much for mortars the neat cement of which worked with 20 per cent makes a fairly wet paste; and that 10 per cent for such a cement gives better results. The reason for this is a physical one, as in tamping a very wet mortar into place, much of the cement is unavoidably lost to the briquettes. During the tamping operation the water is forced to both surfaces, and carries with it the finest (most valuable) cement particles. In finishing the briquette, this top surface, especially rich in cement, is struck off and the resulting briquette is weakened by the reduction of the 1 to 3 ratio as well as by the loss of a portion of its most valuable constituent.

We give this explanation as the reason why many briquette machines fail [22] and why under certain conditions a slight finger pressure will make a stronger briquette than powerful mechanical force. The considerable pressure exerted on the briquettes by such machines forces the water to the surface and this carries cement with it, while the sand is left in the mold.

As the addition or subtraction of as little as 1 per cent of water may effect the resulting strength of a mortar briquette sufficiently to cause the acceptance or rejection of the material, the American Society introduces a good feature in cement testing to cover this effect, for in their specifications the amount of water necessary for any mortar is given according to the percentage of water required to reduce the neat cement to the normal consistency paste. This is shown by the following table:

TABLE XXIII.—*Percentage of water required for standard sand mortars.*

Normal consistency, neat.	1 part cement to 3 parts standard Ottawa sand.
Per cent.	*Per cent.*
22	9.7
23	9.8
24	10.0
25	10.2
26	10.3
27	10.5
28	10.7
29	10.8
30	11.0

[22] *Eng. News* (1902), **48**, 130.

The American Society specifications, with some modifications, will be adopted to test cement for all future Philippine construction work. Although this change has been favored by this laboratory, we do not believe that the above table, regulating the amount of water for mortar briquettes, will be advisable in this climate. A natural, sieved Philippine sand will also be used, but the ratio between the results obtained with this and those with standard Ottawa sand is still to be determined.

Atmospheric influences will not affect the cement during mixing and molding according to these specifications to as great an extent as with the tamping method, as the whole operation of making the briquettes, once the normal consistency has been ascertained, requires only about one-third of the time.

However, the tamping method, according to the United States Army specifications, is more in accordance with actual practice. It takes from sixteen to eighteen minutes to gauge the molds, which is about the average time that concrete manipulation in structural work requires. If the cement begins to set in ten or fifteen minutes, the tensile strength of the briquettes will be reduced by subsequent tamping, which is just what may be expected to happen in field work. According to the American Society manipulation, the briquettes are gauged in five or six minutes, hence the result of quick setting ten or fifteen minutes after the water is added does not affect the tensile strength so much, as the intermingling of crystals which are then formed are not broken up by subsequent tamping. Therefore, failure to pass the initial set requirements of cements tested according to the American Society specifications must be given more important consideration than otherwise, as the tensile strength, while little affected in laboratory tests, may suffer considerably thereby in construction work.

SPECIFIC GRAVITY AND LOSS ON IGNITION.

Much diversity of opinion exists among cement workers regarding the value of the specific-gravity test. It was formerly considered as an almost infallible indicator of adulteration and underburning. The work of Butler,[23] Meade,[24] and of the committee on technical research of the Association of Cement Manufacturers has proved that low specific gravity is often due to seasoning, and that Portland cement can be heavily adulterated and still retain a specific gravity above 3.10. As a result, many engineers do not now attribute any value whatever to this test. However, the experience of this laboratory induces us to support the

[23] *Chem. Eng.* (1907), **5**, 219.
[24] *Chem. Eng.* **6**, 17.

assertion of the paragraph headed "General observations" of the "committee on standard specifications for cement." This committee states:

"Specific gravity is *useful* in detecting adulterations and underburning. The results of tests of specific gravity *are not* necessarily *conclusive* as an indicator of the quality of a cement, but when in combination with the results of other tests *may* afford valuable indications."[25] (Italics are supplied.)

The specific gravity is *useful* in detecting adulterations because certain adulterations will alter the specific gravity beyond the limits of specifications. However, the adulteration of Portland cement is so readily detected by competent chemists and testers that it is now seldom indulged in by manufacturers. The real problem of cement testing concerns itself with the pure product; and for the valuation of this we find the specific-gravity determination to be a great aid. Of course, its importance is limited. Like the chemical analysis, it gives definite aid only to a limited degree. Chemical analysis will not show the degree of burning nor the compounds that exist in a cement; and the specific gravity will not always disclose adulteration or underburning. However, both these tests give valuable aid in tracing causes of defects which by other tests have been found to exist. For instance, it was the relation between the specific gravity, the tensile strength and the setting time of the cement recorded in diagrams 1 and 2 which gave us the first clue to the cause producing the variations which prevailed throughout these tests and which led us more fully to investigate the effects of aëration on high alumina cements. Now that we understand the nature of this cement, the specific-gravity determination alone enables us to predict very accurately what the results of the other tests will be and to suggest how the cement may be improved.

Failure to pass the soundness tests may be due to two causes—excess of lime or underburning. Unsoundness in conjunction with low specific gravity proves that underburning alone is the cause of the warping and disintegrating.

Cements may attain a low specific gravity as a result of prolonged seasoning. If this benefits the cement, well and good; but if it injures it, then the material should not be allowed to season, or, if seasoning has already developed dangerous properties, it should be rejected. The specific gravity, before and after ignition, will indicate to what extent seasoning has effected a well-burned cement, and a record of tests compared with the corresponding specific gravities will show the quality of the cement developed by the absorption of various amounts of water and carbonic acid.

If a cement shows little change in its specific gravity before and after ignition, and also gives unsatisfactory tests in tensile strength and setting

[25] Meade, *loc. cit.*

properties, chemical examination will usually show that it has not the proper "hydraulic index."

Underburned cements usually have a very low specific gravity, because they absorb water and carbon dioxide more rapidly than well-burned cements and because all the carbonic acid may not be driven off during the burning of the raw material. The compounds formed by underburning are not as stable as those of a well-burned cement and hence are more readily influenced by atmospheric conditions.

Underburning is readily detected by the soundness test provided the cement is "fresh;" but seasoning often eliminates the unsoundness and therefore renders this test of no value for its detection. We must then depend upon the specific gravity, loss on ignition, color, and other tests to disclose the fact. A high loss on ignition is not characteristic of the best brand of Portland cement, even after prolonged storage.

R. & W. Fresenius [26] consider "that the limiting value of the loss on ignition of good Portland cement should not exceed 3.4 per cent."

The following table illustrates this contention:

Conditions.	Cement A.		Cement B.		Cement C.	
	Specific gravity.	Loss on ignition.	Specific gravity.	Loss on ignition.	Specific gravity.	Loss on ignition.
Not quite fritted	2.92	3.59	3.04	1.47	2.92	5.39
Slightly fritted	3.105	0.66	3.15	0.59		
Strongly fritted	3.115	0.27	3.18	0.19	3.00	2.36
Very strongly fritted					3.19	0.24
Overburned	3.05	0.65	3.05	0.28		

Sabin [27] remarks "that the determination of water and CO_2 may give some idea of the deterioration of a cement on storage. M. Candlot considers that in the case of Portland cement a loss on ignition (water and CO_2) exceeding 3 per cent indicates that the cement has undergone sufficient alteration appreciably to diminish its strength. Spalding [28] affirms that "if the quantity of CO_2 be large, it indicates either that the burning has been incomplete or that the lime has become carbonated by subsequent exposure. The energy of the lime is thus diminished, the portion of lime in combination with CO_2 being inert."

While we have not enough data to cover every instance and to formulate this as a general rule, it has been our experience that the absorption of carbonic acid and water decreases the tensile strength of every *sound*

[26] *Soc. Chem. Industry* (1894), **13**, 252. *Ztschr. Anal. Chem.* (1893), **32**, 433, 445.

[27] Sabin, Louis Carlton: *Ibid.*, 34.

[28] *Ibid.*, 4.

Portland cement, even though it does not develop quick-setting properties by this exposure. Table XXIV gives a typical example:

TABLE XXIV.—*January 22, 1907—mortar, 1 to 3.*

[Specific gravity, 3.11.]

	7-day.	28-day.	Number of briquettes broken.
Average	171	227	12
Highest	195	250	12

This same cement stored in coarse canvas cloth bags, twenty days and three months longer, gave the following results:

[Specific gravity, 3.03 after 3 months.]

	7-day.	28-day.	Number of briquettes broken.
After 20 days:			
Average	147	212	12
Highest	165	230	12
After 3 months:			
Average	135	200	16
Highest	146	211	16

From the nature of things this loss in tensile strength is not difficult to explain. It is generally understood that all cements are improved by storage, but it has been proved that this is only true of those cements which are either too high in lime or underburned. Aëration renders part of the excess or free lime inert because of the formation of the carbonate of calcium and also slakes some of it by the absorption of water. Thus, the cause of unsoundness is removed in time, and the cement is gradually improved in this respect. But "the higher in lime a cement is the greater its strength is known to be if thoroughly burned,"[29] and "the maximum of lime is usually controlled by the soundness tests."[30] Therefore, if a cement is sound it does not contain excess or free lime and the carbonization of the lime in a sound cement should reduce its tensile strength, as it lowers the percentage of *active* lime, the carbonate of calcium being inert.

With all due respect for the great value of Meade's work, we take exception to a portion of his assertions relative to the specific gravity.

[29] *Eng. News* (1905), **53**, 84.
[30] *Chem. Eng.* (1907), **5**, 343.

Among other conclusions he states [31] "that low specific gravity is usually caused by seasoning of the cement or of the clinker, either of which improves the product. * * * Underburned cement is readily and promptly detected by the soundness tests and no others are needed for this purpose. * * * That the requirements of specific gravity should be omitted."

Underburning is readily detected by the soundness test, only when the cement is fresh. Seasoning of underburned cement may eliminate the causes of its unsoundness. Meade himself states in this same reference that an underburned cement which, when freshly made, failed to stand a 5-hour steam test without complete disintegration, after one month's seasoning stood 5-hour steam and boiling tests perfectly. The greater part of the cement received at this laboratory for commercial testing has been seasoned for a greater or less length of time, therefore the soundness tests are not liable to detect underburning in most instances.

Cement raw material, high in alumina, fuses so readily that it is difficult to control its burning, and as a result almost all high alumina cements vary considerably. It is also very difficult to detect the relative degrees of burning which the commercial, high-alumina cements have undergone and it is only possible to do so by taking into consideration many of the physical properties of the material. It has been observed that a brown shade,[32] a low specific gravity,[33] a high loss on ignition, the presence of blotches [34] between the soundness pat and the glass plate, a high, insoluble residue and a generally erratic behavior of a cement, exist simultaneously with a relative increase in the rate of carbonic acid and water absorption. These are all regarded as signs of underburning, and a study of all of them gives the only indications of the relative degree of burning of seasoned, high-alumina cements that we have been able to recognize.

Meade's statement that seasoning of the clinker improves a cement is also open to discussion. Some cements are improved by this procedure, but many others are not. Instances are on record where seasoning induced quick setting and low tensile strength, even when calcium sulphate was present. Meade admits "that cements should contain at least 2.5 times as much silica as alumina. Cements containing less than this amount of silica are apt to be quick setting, or else to become quick setting on exposure to air."

It is hardly necessary to state that we do not think that the requirements of specific gravity should be omitted from specifications. This

[31] *Ibid.*, 6, 19.
[32] Sabin, Louis Carlton: *Ibid.*, 36.
[33] *Soc. Chem. Industry* (1894), 13, 255.
[34] Taylor and Thompson: *Ibid.*, 101–107.

test is of great value under certain conditions. Every good Portland cement will meet its requirements before or after ignition, and therefore its determination imposes no unjust or partial test.

Determination of the specific gravity will be valueless unless the effects of aëration are guarded against, as the exposure of the small quantity of cement necessary for this test enables the action of the atmosphere to alter its composition very much in a short time and so to reduce its specific gravity accordingly.

It is the practice of this laboratory to take the cement for the specific gravity determination from the sample at the same time that the material for the other tests is taken. It is then dried at 110° for thirty minutes and immediately put into small, glass bottles which are tightly corked until the cement has cooled; it is only used after this procedure.

The difference between the specific gravities before and after ignition indicates the amount of volatile constituents present in the cement, but when it is desired to know only the amount of carbonic acid and combined water which has been absorbed, the loss on ignition affords a much simpler and a more accurate test.

CLIMATIC INFLUENCES.

Local, tropical, climatic conditions must necessarily have an influence upon cement and cement testing. In the tropics, all work is done practically in the open air, being protected only from the direct rays of the sun. The climatic conditions under which cement tests or commercial work are undertaken coincide very closely with the meteorologic observations which are given in the following table for the year:

TABLE XXVI.—*Summary of meteorologic observations taken at Manila,*[a] *P. I., situated on the west coast of the Island of Luzon.*

Month.	Temperature.						Mean relative humidity.	Average rainfall.	Average number of rainy days.	Mean cloudiness.
	Mean.		Maximum.		Minimum.					
	°C.	°F.	°C.	°F.	°C.	°F.	*Per ct.*	*In.*		*Per ct.*
January	25	77	33.9	93	16.7	62	78	1.19	5	4.6
February	25.5	78	35.6	96	16.1	61	74	.41	3	3.8
March	26.6	80	35.6	96	17.2	63	72	.74	3	3.8
April	26.3	83	37.2	99	18.9	66	71	1.14	4	3.5
May	26.3	83	37.8	100	21.7	71	77	4.20	9	5.1
June	27.8	82	36.1	97	21.7	71	82	9.62	16	6.8
July	27.2	81	35	95	21.1	70	85	14.57	21	7.5
August	27.2	81	34.4	94	20.6	69	84	13.87	20	7.5
September	26.6	80	34.4	94	21.1	70	86	14.93	20	7.4
October	26.6	80	35	95	20.6	69	83	7.54	16	6.1
November	26.1	79	33.3	92	18.3	65	82	5.13	12	5.8
December	25	77	33.3	92	15.6	60	81	2.13	8	5.6

[a] "The climate of Manila is hot and moist during the greater part of the year. During the spring months it is dry. The afternoon temperature of the hottest portion of the year is modified by the northeast trade winds that prevail at that season." Brewer, Isaac W.: Personal Hygiene in Tropical and Semi-Tropical Countries (1908), 119.

All the requirements of standard American cement specifications are based upon cement action characteristic of a colder climate. It would be possible, of course, to manipulate the cement testing itself in tropical countries at the temperature limits specified in American standards; but this could only be done at great inconvenience and at a large expense and furthermore it would not be practical, as the results of tests so conducted would not be true criteria of the behavior and value of the cement when used in construction work. The allowances and requirements due to the effect of the relative difference in temperature between temperate and tropical climates should therefore be taken into account in local cement specifications.

During the past year this laboratory has received a number of letters upon this subject from manufacturers, engineers, contractors, testers and other cement workers. These either request information or make statements regarding the influence of local climatic conditions upon various phases of cement action and manipulation. A diversity of opinion has been expressed in regard to the effect of these influences by men familiar with cement work, and probably this is due to the fact that Portland cement is a very variable product and therefore local conditions which would improve the quality of one brand would injure another, and vice versa, and during the past year our endeavor has been to secure a sufficient number of results with various brands of cement to throw some light on the effect produced by this climate on the tests.

Careful cement testing with due consideration of all conditions is of the greatest importance in a country such as this, where much of the material comes a long distance by sea, and where the rejection of a shipment means a proportionately greater loss to the dealer, owing to the cost of transportation, and also to the engineer, as construction work may be delayed. On the other hand, construction work is very expensive in this Archipelago and therefore a rigid interpretation of specifications is necessary to provide against all possibility of the use of dangerous cement.

Contrary to the general belief, the difference between local climatic conditions and those of the temperate climates exerts very little influence upon the usual standard Portland cement tests themselves. Provided the cement is of good quality the warmer temperature prevailing here usually tends to give higher results. Of course, the fineness is not affected by it, and the specific-gravity determination is made independently of the surrounding temperature. The "accelerated soundness" tests especially, are benefited, as the cement does not suffer as great a change in temperature; and hence expansion and warping is not so marked. Climatic conditions improve the characteristics of early tensile strength of most cements, as the variation in temperature from day to day and from hour to hour is only slight, the temperature of the water bath is higher than in cold climates, and the temperature during gauging

is also higher; these are all factors conducive to the development of high early strength.[35] Comparative tests of both sand and neat briquettes made and preserved in the cold-storage room (17° to 21° C.) and also in the laboratory (26° to 30° C.) gave almost without exception lower results, from 3 to 10 per cent, at the lower temperature. The briquettes broke more uniformly when made at the colder temperature. The difference between the strength developed under both conditions was always slight and within the limits of personal error.

However, the relatively high temperature of this climate will seriously effect the setting properties of some Portland cements. This is illustrated by Tables XV and XVI (pp. 152 and 153). Fortunately, the setting properties of the majority of cements are only slightly influenced by this difference in temperature (Tables XIV and XVII). It is the experience of this laboratory that high alumina cements develop setting qualities characteristic of class 2 (Tables XV and XVI); further experimented work is necessary to determine whether this phenomenon holds true only with this class. When comparatively fresh, high-alumina cements set slowly at both temperatures (Table XIV), additional seasoning renders them slow setting at first at 17° to 21°, but quick setting at 29° to 31°, and finally quick setting at both temperatures.

The development of quick setting is marked by other peculiar characteristics. When the absorption of carbonic acid and combined water has progressed sufficiently, no practical amount of water which can be added will retard the rapidity of setting or eliminate the early generation of much heat, but in the earlier stages of seasoning a variation of as little as 0.5 per cent of water in mixing may produce a most remarkable difference in the time of the initial and final sets. This is shown by the following table:[36]

TABLE XXV.—*Showing the effect of varying amounts of water on the time of setting.*

Sample No.	Water.	Condition.	Initial set.	Final set.
	Per cent.		*h. m.*	*h. m.*
F5-1	21	Becomes dry and noncohesive; heats up 6° in 4 minutes	([a])	([a])
F5-1	22	Just plastic enough to mold	0 15	1 10
F5-1	23	Plastic	1 10	2 25
F5-3	22	Just plastic	20	1 10
F5-3	23	Plastic	1 30	2 25
F5-5	22.5	do	15	30
F5-5	23	do	1 15	2 20

[a] Impossible.

[35] *Annual Report Chief of Engineers, U. S. A.* (1894), 234. Sabin, Louis Carlton: Cement and Concrete, New York (1905), 119–120. Alexandre, Paul: Recherches Experimentales sur les Mortiers Hydrauliques.

[36] See also Table XVII of this paper.

The samples were well mixed and screened before testing; troweling was done as uniformly as possible for exactly five minutes; the atmospheric and moist-closet exposure was the same in all cases, except that there was a gradual change in temperature from 27° at 8 a. m. to 29° at 2 p. m.

After troweling sample F5-1 with 21 per cent of water for about four minutes, it suddenly became hot and dry, crumbling apart. No amount of patting would cause the cement to stick together sufficiently to form a pat.

The same result was observed on repeating the operation, and a thermometer placed in the mass rose 6° in four minutes. However, upon adding 22 per cent of water to the same cement no rise in temperature was observed during troweling; the resulting paste was sufficiently plastic to be easily molded into a pat; and the needle used for the initial set when first applied, sank about one-eighth of an inch. However, five minutes after the pat was placed in the moist-air closet, it began to heat and to dry slightly, the initial set taking place in fifteen minutes. This experiment was repeated with similar results. Twenty-three per cent of water was then used. The plastic paste, when formed into a pat, acted normally in every way and gave a satisfactory setting time.

The results obtained with sample F5-3 and F5-5 were practically identical. In the case of the latter, the excess percentage of water was reduced by 0.5 per cent to determine if possible the minimum quantity necessary to effect so profound a change.

Two important facts become evident from the above data, namely, that both the plasticity and setting time of a cement, such as was being tested, are much affected after a certain quantity of water has been added by the subsequent addition of even very small amounts of the solvent.[37]

We are not prepared to discuss fully these results at the present time, but their analogy to the phenomenon of the crystallization of certain salts from solution is striking. Many salts have a critical solution factor. Under slow evaporation they will remain in solution until a certain limiting percentage of the solvent has been reached, when the salt will crystallize almost instantly, heat being generated during the separation. A cement, the setting properties of which are so profoundly affected by the addition of even small quantities of water, may be said to have a critical solution (or hydration) point. We would hesitate to decide whether such a cement deserves to be approved. If tested according to the United States Army specifications it would fail to pass the setting test, but under those of the American Society the normal plasticity method will give it sufficient water to cause it to set slowly.

An engineer in these Islands related an experience illustrating the practical importance of this problem. The mortar, after mixing, was dumped into a car and transported to its destination by rail in five minutes. Working with a large shipment of this cement no difficulty was experienced for some time, but finally when one carload reached its

[37] This same phenomenon is less delicately shown in fig. 19 of Taylor and Thompson "Concrete, Plain and Reinforced." It will be noticed that Portland cement *C* (without gypsum) reached its final set even in less than thirty minutes with 20 per cent of water. With 25 per cent of water the initial set took one hour and thirty minutes and the final set five hours.

destination the cement had set so hard that it was removed from the car only with much difficulty. He attributed this change to the variability of the cement, but we are inclined to believe that the water added was just sufficient to bring the cement to the critical solution or hydration point and that a bucket or so of water less than was usually employed, was used in mixing, and quick setting was the result.

Portland cement is most affected by local climatic conditions before and not after it is gauged. High temperature and the alternating humid and dry atmosphere are conditions under which hydration and carbonization are accelerated. In consequence, the majority of commercial products must be especially prepared to withstand tropical climates. Portland cement is very susceptible to changes under these conditions, and it is therefore essential to the best practice that cement intended for use in the tropics should develop no dangerous properties by the absorption of water and carbonic acid in normal quantities. The cement problem of tropical countries depends for its solution upon the characteristics of Portland cement; and our efforts have been to determine what class of cements are least injuriously affected by exposure and seasoning.

We believe that high-alumina cements are least efficient for use in tropical climates, although they have one laudable feature in that they never show the slightest inclination toward warping or disintegrating. Air, steam and boiling tests always develop perfect soundness. This is probably due to the fact that aluminous raw material fuses very readily at a comparatively low heat. "Lime burned at a high heat slakes much more slowly, and is therefore more likely to be injurious than when burned at a low temperature." [38]

Aluminous cements gain most of their strength very quickly. "The aluminates are thought to contribute little to the final strength of the mortar, as they are not permanent compounds, but are acted upon by various salts with which they are likely to come in contact in the work. For this reason they are not adapted for work exposed to the action of air and sea water." [39] "The aluminate acts in a very energetic manner upon the set, but very little upon the hardening which is caused by the silicate of lime." [40] Also "from the character of the silicates and the aluminates it is evident that the latter are acted upon more quickly and rapidly than the silicates, and it is to the crystallization of the lime from the aluminates that the initial set must be contributed. Subsequent hardening must be due to the liberation of lime from the silicates." [41]

In conformity with these quotations, it has been our experience with cements of this nature that the 7- to 28-day gain is small; that satisfactory 7-day breaks do not insure satisfactory 28-day strength; that 7-day strength may be even greater than 28-day; that little gain

[38] Spalding, Frederick C.: *Ibid.*, 73.
[39] *Ibid.*, 54.
[40] *Ibid.*, 58.
[41] Clifford, Richardson: *Eng. News* (1905), **53**, 984.

in strength takes place after twenty-eight days and instances are on record where the strength of the briquettes weakened after three months. The fifty samples illustrated in diagrams numbered 1 and 2 show only an average gain (seven to twenty-eight days) by the testers, of 16.45 per cent for neat and 48.9 per cent for sand briquettes, whereas the increase desired by the Army specifications is at least 20 and 57 per cent, respectively (Table I). "Cement giving high early strength is to be relied upon only in so far as it has been shown by experience that it is capable of maintaining such strength." [42]

The fact that the early strength of this class of cement can not always be relied upon is probably due to its nonuniformity in burning. Owing to the fusibility of the calcium aluminate, which causes balling-up and sticking together in the hot zone of the kiln,[43] thus preventing uniform burning, cements high in alumina are apt to be very erratic in the stability of their compounds. As a result the rapidity with which they unite with water and carbonic acid when exposed to the atmosphere varies. The relative rapidity of the absorption of carbon dioxide and water by cements under similar conditions would therefore indicate the relative degree of low burning.

The most important characteristic of a high-alumina cement and the one that needs the most consideration is its susceptibility to become quick setting by exposure to the air. It has been our universal experience that Portland cements of this class containing more than 8.5 per cent of alumina always gave satisfactory results if they are tested before they have combined with more than 2 per cent of water and carbonic acid; and that when they had combined with more than 3 per cent of volatile constituents they failed to meet the setting and tensile strength requirements.

It would seem as if there is something radically wrong with a cement that will not withstand atmospheric exposure to such a slight extent without developing dangerous properties, and such a cement should be rejected for use, especially in this climate. A typical example, sample No. 8 as recorded in Tables VII and VIII, will suffice to illustrate this.

It is difficult perhaps to realize why such a slight difference in volatile constituents should so change the quality of a cement; and that the same cement which at first set in one hour and thirty minutes (loss on ignition=2.63 per cent) should, after a little more aëration develop such rapid setting properties, and set in twenty-three minutes (loss on ignition=3.92 per cent).

The combination of Portland cement with water and carbonic acid absorbed from the air is represented for all purposes of discussion by the

[42] Spalding, Frederick C.: *Ibid.*, 88.
[43] Meade: *Chem. Eng.* (1907), 5, 345.

quantity of water necessary to slake the lime, if all were present as calcium oxide, and to combine with the slaked lime to form calcium carbonate, regardless of any intermediate reaction on other compounds which might be present. This change can therefore be represented by the following equations:

$$CaO+H_2O=Ca(OH)_2$$
$$Ca(OH)_2+CO_2=CaCO_3+H_2O$$

or,

$$CaO+CO_2=CaCO_3$$

and therefore, 1 part by weight of water will unite with 3.1 parts of lime to form 4.1 parts of slaked lime, and one part of carbon dioxide will unite with 1.5 parts of lime to form 2.27 parts of calcium carbonate.

From the above equations it is very apparent how an otherwise unsound cement is improved by the absorption of 3 or 4 per cent of water and carbonic acid. Excess of free lime causes the unsoundness and the more of this lime which is slaked or rendered inert before gauging the cement, the sounder the resulting product will be. The calcium silicates being much more stable compounds than the calcium aluminates, the latter would be acted upon first by climatic influences. The addition of lime or slaked lime to a cement retards the setting, and from the nature of the reaction, quicklime would retard the setting more than slaked lime. The natural tendency then of the lime is to off-set the quick setting properties of the aluminates. Other conditions being the same, anything which tends to reduce the activity of the lime in a slow-setting, sound cement, will increase the rate of its setting. The ignited cement of sample No. 8 had the following composition:

	Per cent.
Silica (SiO_2)	20.5
Alumina (Al_2O_3)	8.6
Iron oxide (Fe_2O_3)	2.8
Lime (CaO)	65.4
Magnesia (MgO)	2.3
Sulphuric acid (SO_3)	0.4

Table VIII shows that the cement from the bag had absorbed 0.50 per cent more carbonic acid and 0.79 per cent more combined water than that in the can. It therefore contained (equation 3) 1.13 more inert calcium carbonate and 3.24 per cent (equation 1) more slaked lime; or 0.75 per cent (equation 3) of the lime present in the raw material had been rendered inert, and 2.45 per cent had been slaked by the additional absorption of combined water and carbonic acid by the same cement stored in the bag.

The lime in combination with silica must be left out of this consideration as the silicates of calcium exert practically no influence upon the initial setting properties of the cement. The entire loss in active lime

affected the equilibrium maintained in the early setting properties by the opposing forces of the aluminates and the lime not in combination with silica. Therefore, a loss in the activity of this lime representing 0.75 per cent of the total cement of sample number 8 affects this equilibrium to a degree many times greater than if the silicates would need to be taken into consideration.

Synthetic experiments also show this same phenomenon. "If much more than 10 per cent alumina is present the cement is almost sure to be quick setting even with the addition of sulphates." [44] "When cement treated with sulphate of lime has regained quick set, it may again be made slow set by addition of a small quantity of lime." [45]

Our belief that this cement is not of good quality is also supported by universal experience. We have already stated that this class of cements gives satisfactory tests when the samples are comparatively fresh, but fails to do so after seasoning. It will be noted that the percentage of alumina and silica in sample number 8 satisfies the limits of R. K. Meade's formula for "freshly made American Portland cements which pass standard specifications for soundness, setting time, and tensile strength," [46] namely:

	Per cent.
Silica	20–24
Alumina	5– 9
Iron oxide	2– 4
Lime	60–63.5
Sulphur trioxide	1– 2

However, they do not fall within the limits of Le Chatelier's formula for "the limits of the amount of material usually present in good commercial (therefore seasoned) Portland cement,[47] that is:

	Per cent.
Silica	21.0–24
Alumina	6 – 8
Iron oxide	2 – 4
Lime	60 –65
Magnesia	0.5– 2
Sulphur trioxide	0.5– 1.5
Water and carbonic acid	1 – 3

The percentage of sulphur trioxide is also lower than that given by both authors; and the loss on ignition is greater than that given by the formula which considers it.

Furthermore, Meade states that "cements should contain *at least* 2.5 times as much silica as alumina. Cements containing less than this amount are apt to be quick setting or else to become quick setting on

[44] Meade: *Chem. Eng.* (1907), **5**, 345.
[45] *Ibid.*, 349.
[46] *The Chem. Eng.* (1907), **5**, 349.
[47] *Trans. Am. Inst. Min. Eng.* (1893).

exposure to air." Sample number 8 contained 2.38 times as much silica as alumina, and its actions supports Meade's conclusion.

Cements which contain less alumina and more silica than sample number 8 withstand exposure much better. All of the five different cements recorded in Table XXVI below, failed in setting time and tensile strength when their seasoning had progressed as indicated by the "loss on ignition" column. However, number 5 withstood aëration the best. It was only after it had stood exposed to the air for a very long time and had united with 6.36 per cent of water and carbonic acid that it failed.

TABLE XXVI.

Constituent.	Cement 1.	Cement 2.	Cement 3.	Cement 4.	Cement 5.	Cement 5, ignited.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Silica (SiO_2)	20.65	20.70	22.0	20.52	21.28	22.9
Alumina (Al_2O_3)	8.57	8.42	8.9	8.71	6.95	7.5
Iron oxide (Fe_2O_3)	3.07	3.01	3.0	2.65	2.29	2.5
Lime (CaO)	61.83	61.60	59.9	61.30	61.08	65.7
Magnesia (MgO)	2.26	1.94	1.55	1.96	0.21	0.2
Moisture (110°)	0.41	0.34	----------	0.88	0.72	----------
Loss on ignition (water and carbonic acid).	2.47	2.76	5.3	4.33	6.36	----------
Sulphuric acid (SO_3)	0.51	0.59	----------	0.46	1.17	1.26
Carbonic acid (CO_2)	0.78	0.43	----------	3.04	4.36	----------

Seven and 28 day mortar briquettes (1 to 3), as the seasoning of the cement progressed, gave the following tests of tensile strength:

7-day.	28-day.	Loss on ignition.
		Per cent.
236	320	2.97
187	247	4.53
172	211	6.36

Contrary to this behavior, number 4 gave the worst results and a very plastic paste made from it set in fifteen minutes with a rise in temperature from 29° to 38°.5 C. Cements numbered 1 and 2 showed only 2.47 and 2.76 per cent loss on ignition respectively and yet they were quick setting.

By further investigations of this nature we hope to prove what brands of Portland cement in particular are best suited to withstand tropical climatic influences best. At present we feel justified in drawing the following conclusions as being conducive to the best results and practice for all cement operations in this and similar regions.

CONCLUSIONS.

1. We believe that the composition of Portland cement best adapted for use in tropical climate should be within the following limits:

	Per cent.
Silica	22 –24
Alumina	5 – 7
Lime	62 –65
Magnesia	0.0– 4
Sulphur trioxide	1.0– 2
Water and carbonic acid	0.5– 3

2. "Soundness" in accelerated tests deserve special attention here, because of the prevailing high temperature. Perfect soundness is especially important for concrete works which are exposed to the intense heat of a tropical sun.

3. "Underburning" is fatal to the efficiency of Portland cement to be used in the Tropics, as the unstable compounds so formed are most easily attacked and decomposed by the energetic atmospheric influences.

4. All "sound" cements should be protected from additional aëration as much as is practicable, as otherwise quick setting or low tensile strength is liable to be developed.

5. Sound and well-burned cements, high in silica and low in alumina, will withstand climatic influences best both before and after gauging.

6. High alumina cements give fairly satisfactory results if they are used before they develop quick setting. Quick setting is sure to develop in such cements if they are exposed to the air for any considerable length of time.

7. Samples sent to the testing laboratory should be preserved in packages which thoroughly protect the cement from the atmosphere. No accurate results consistent with the quality of the cement as it exists in the barrel at the time of sampling will otherwise be possible. Setting tests made at the laboratory before and after exposure should be insisted upon, and if quick setting develops by this additional seasoning the cement should be rejected.

This work will be continued and our effort will be to secure samples of as many grades of cement as is possible, in order more thoroughly to test the soundness of these conclusions.

EDITORIAL.

PERIDINIUM.

For a number of years the Bureau of Health has received many complaints from the residents of Bataan Province to the effect that the dumpings from the sanitary barge *Pluto* caused a great mortality among the fish along the shores of that province. An investigation into the matter, conducted by Deputy Commissioner H. M. Smith of the United States Fish Commission steamer *Albatross,* proved that the mortality among fish is in no way connected with the *Pluto* but is due to visitations of *Peridinium* in Manila Bay. The following is taken from a report on this subject by Dr. Smith:

There have been at least three visitations of *Peridinium* in Manila Bay during the current year, a noteworthy one occurring in the latter part of January. The discoloration of the water at that time was observed about the 23d of the month, and increased in intensity until the 26th or 27th, after which it rapidly diminished and practically disappeared from the head of the bay by the 31st. Another visitation was observed during the third week in March but was less extensive than the foregoing.

Whenever *Peridinium* has invaded Manila Bay, the water over large areas has been made turbid by minute protozoa, and at a distance has the peculiar pale reddish color characteristic of such invasions. When the water was viewed over the side of the *Albatross,* another color was seen; and a very pronounced iron-rust tinge was observed when the animals were closely packed. The rusty color was found to be due to contained chlorophyl. At times, dense masses of *Peridinium* floated past the *Albatross* in wavy bands several yards wide and hundreds of feet long.

During the prevalence of these invasions, the bay is unusually phosphorescent, and tests show that the *Peridinium* is the chief cause of the luminosity. A tumblerful of water taken at night alongside the *Albatross,* and found to be thick with the organisms to the exclusion of all other creatures, glowed brightly with a blue light when carried to a dark room and agitated.

Whenever *Peridinium* has appeared in the bay, there has been a remarkable scarcity of other forms of animal life. The dense schools of small fish (*Atherina* and others) which are nearly always present in the surface waters of the bay, and are so conspicuous about the wharves and

vessels, disappear completely, and with them the larger fishes that prey thereon. For a number of days not a living thing of microscopic size can be seen at the surface of the water, and fish-eating birds also disappear. As the amount of *Peridinium* diminished, the small fishes gradually reappear in the open waters (coming either from the bottom or from places where streams enter the bay and render the water unsuitable for the protozoän). The gulls and terns also return. Finally, when the creatures have practically withdrawn, the small fish reappear in myriads.

A small, salt-water aquarium on the *Albatross,* containing a number of different kinds of fishes and mollusks from points south of Manila, was in a very flourishing condition when the ship entered the bay one morning several weeks ago, but the same night nearly all the fishes and mollusks were killed, and examination showed myriads of the *Peridinium* on the gills, etc. The few fishes that survived were rapidly succumbing, until the water supplying the aquarium was strained through a fine-meshed bolting cloth, thus eliminating the injurious organisms. Since then the fishes have been quite healthy.

During the prevalence of this pest, the Manila markets contain much less fish than normally, and many stalls are entirely vacant. Inquiries among the fishermen show that there is a decided falling off in the catch and that some dead fish are reported in the *baclods.* The injury done to the fish, however, appears to be much less than might be expected, the known mortality among aquatic creatures being so small as to afford a noteworthy contrast to the ravages of *Peridinium* in America and Japan.

AN ACCOUNT OF A HUMAN SACRIFICE HELD BY THE BAGOBOS, DISTRICT OF DAVAO, MINDANAO, P. I.

A geological reconnaissance of the Island of Mindanao and the Sulu Group was begun by the division of mines of this Bureau in September, 1907. The scientific work was under the direction of W. D. Smith; the military escort which was necessary throughout most of the work was commanded by Lieut. Charles S. Caffery, Second Infantry, United States Army. One part of this work consisted in an expedition from Kotabato to Davao, a distance of over 200 miles, 90 of which were covered by a sternwheel boat plying up the Rio Grande, or Pulangi, River, from where the party traveled overland across the Matutan and Apo Ranges to Davao Gulf. This party formed the second expedition of white men to make this entire trip.

The region west of the divide is inhabited by Moros, Mohammedan tribes in a semipacified state, and Manobos and several other pagan groups live in the region on the east of the divide. Several tribes or subtribes are to be found on the slopes of Mount Apo, among which may be men-

tioned the Atas, Giangas, Bagobos and the Kalagans. Several Americans and Spaniards have visited the people around Davao Gulf and have studied their ethnology. The Jesuits devoted themselves for many years to missionary work in Mindanao and much of scientific value was accomplished by this learned and able body of men. Mr. Frederick Sawyer has gleaned more or less scattered information from their "letters" which he has included in his book "The Inhabitants of the Philippines,"[1] in which he merely refers to human sacrifices without giving any of the details, and these references are to sacrifices held only among the Giangas and Tagakaolos. Blumentritt[2] says even less about the Bagobos, and furthermore, he never saw any of the people of the Philippines about whom he wrote. No work has yet been carried on among these peoples by the division of ethnology of this Bureau and as it may be some time before any attempt will be made to study them, I have obtained permission from the chief of that division to contribute some interesting data regarding some of their customs.

We encountered Bagobos along the route for several days after we reached the Matutan Range and some of them made the trip into Davao with us; when we made the ascent of Mount Apo we spent several nights in their villages and used the people for guides and carriers. The large man in the center of the group, shown by Plate I, is Tongkaling, the chief of all these people, surrounded by some of his dependents. Tongkaling is a headman and wears the badge given him by the authorities of the Moro Province. Plate II is a view of the chief's house. Although the Bagobos wage petty wars among themselves, they have caused little trouble for Americans. Indeed, many of those nearer the coast work on the American plantations and do fairly well.

The men of this tribe present a better appearance than do the women, and in physique and features they surpass most of the other natives in the Archipelago whom I have seen, and I have seen many of the tribes. It is said that, like the ancient Spartans, they strangle at birth all deformed children. Their hempen garments are highly decorated with shell ornaments and with Italian beads which they procure from the Chinese. They mark with some sort of design nearly every article they use, as can be seen by examining the old chief's shield and spear. The men are greatly addicted to the practice of tattooing; the women are not tattooed to any extent, but wear brass rings on their fingers, ears, necks, toes and ankles.[3]

The *agong,* shown in the upper left-hand corner of Plate I, is known and used all over the Malay region. I have seen one man play on as many as six of these at a time. It is the chief musical instrument in

[1] Sawyer, F. H.: Inhabitants of the Philippines, Charles Scribner's Sons, New York (1900), 353.

[2] *Globus* (1882), 42, 219–222; *Globus* (1897), 71, 19–20.

[3] Anyone traveling in the Bagobo country will do well to lay in a stock of beads, brass wire and cheap jewelry.

these districts, is made of brass and is imported from Singapore. *Agongs* cost from 20 to 50 pesos Philippine currency each and are the measure of a man's wealth. Tongkaling had forty of these hanging about in his house at the time I visited him. In addition to the *agong,* the Bagobos have a rude drum, not essentially different from any other drum, a bamboo fiddle and a reed flute. The music is exceedingly simple and monotonous.

The entire system of living among the Bagobos is feudal, and slavery is practiced among them. The man shown in the extreme left in Plate I is a Bilan, and judging from the treatment received by him at the hands of the Bagobos, it is not hard to believe that he is a slave. These people do most of their traveling on horseback, riding very sturdy little ponies, usually adorned with bells which they buy from the Chinese and which they also use to decorate their clothing and pouches. The Bagobos have been aptly termed "horse Indians."

It is not my intention to present here a complete account of this interesting people, as I have had neither the time to study them nor the necessary training as an ethnologist to enable me to do so. However, I wish to give some interesting information which I obtained from Governor Allen Walker, of the district of Davao, relating to a most interesting tribal religious custom. The special event which I am about to relate took place the week before we arrived in the town of Digos, but before presenting this account it may be well to give a few extracts from the Jesuit letters bearing on this religious custom.

Mr. Christie, of the division of ethnology of this Bureau, in searching through the letters written by the Jesuit missionaries in Mindanao, found references to human sacrifices. These references are in letters dated in the years 1885 and 1886. They have not been copied *verbatim,* but synopses are given. The first letter, that of Father Gisbert to the Father Superior, dated Davao, April 2, 1885, says, in substance:

> The Bagobos have been making more human sacrifices, notwithstanding their promises to the contrary and the vigilance of the writer. A slave girl from Cauit mission, named Padal, was sold and sacrificed; also a pagan named Maguana. "Captain Atas" also made a sacrifice a short time ago.

The second letter from the same father to the fathers and brothers at Veruela, dated Davao, January 4, 1886, contains the following interesting information:

> The Bagobos have two feasts a year, one before planting and the other after harvesting. The latter is innocent enough, and is known as the "women's feast." All gather in the house of the headman late in the afternoon, where they eat the best to be had and drink a beverage of fermented sugar-cane juice. They also have instrumental music, singing and dancing, and the party usually breaks up about morning
>
> The other feast is quite different, and though comic in some of its details, is in its principal part, tragic, criminal and disgusting. The tragic part comes

first; the people gather in some dense forest, taking all necessary precautions that the authorities and missionaries learn nothing of their doings or whereabouts. They take their victim, usually a slave, and tie him securely. Then, knives in hand they dance around him hacking him until he is dead. During this operation they shriek like maniacs, provided they are not too close to a Christian settlement, or otherwise likely to be discovered. If they think they are in danger of discovery they gag their victim, refraining from all noise. Then they retire to the headman's house, carrying branches in their hands which they later place in a big joint of bamboo. This is the altar and is the only thing approaching an ornament about the place. Here they eat, drink, dance and play innocently enough. At this point an old man, usually the headman, assumes the principal part. He sits by the altar, takes a glass of their wine in his hand, and, in company with his companions, addresses the "great devil," whose feast they are all celebrating, as follows:

"Darago, we celebrate this feast in your honor both willingly and joyfully, and we offer you the blood of the victim, together with this wine which we drink, so that you may be our friend and accompany us and assist us in our wars."

This being said, they recite a form of litany in which all the most noted *Daragos* known to them are mentioned, the whole assembly reciting these names in unison.

The Bagobos believe in a future state, and hold that each person has two souls. God, or *Fiquiama*, is very good, they say, and he made all things, although it is true that he was assisted by some minor gods who are subject to his order. These minor gods are *Mamale*, who made the earth; *Macacoret*, who made the air; *Damacolon*, who made the mountain; and *Macaponguis*, who made the waters. One of the two of each individual's souls goes to hell and the other to heaven; for they believe that the devil has to do with them in the next world as well as in this, and they give him about equal rights with God. They hold that the devil is very bad, likes blood, and is the cause of all disorder. Thus, they forget good and in all things serve and adore the devil. When a couple of rank marry, there is a human sacrifice to keep away sickness, etc., all of which calamities are attributed to the devil. When a contagious disease makes its appearance, or when there is fear of approaching death, a great gathering is held for the purpose of arranging a human sacrifice and praying to the devil to let them live in consideration of this generous offering.

According to Bagobo customs, the proper time for a sacrifice is when a member of a family dies, and before the termination of the "Lalaoan" or mourning. At such a time a sacrifice is announced much in the same way as Christians would proclaim a feast day or a pilgrimage. At the appointed time all assemble in a place agreed upon, or at least one person from each family in mourning. Their numbers frequently reach fifty or more persons. There is then an assessment to cover the purchase price of a slave and he who pays the largest part is allowed to strike the first blow. Usually the victim cries out while he can and begs for mercy, but his voice is lost in the shrieking of his assassins who make one of the most horrible uproars imaginable. As has been said, when a sacrifice is made near a Christian community there is no shouting and the victim is gagged.

The third letter from Father Gisbert to the fathers and brothers at Veruela, dated Davao, February 8, 1886, continues an account of Bagobo customs:

How did the writer of the foregoing letter acquire so exact a knowledge of Bagobo custom? True, he did not witness a human sacrifice; but the account

given by him in the preceding letter was furnished by baptized Bagobos and also by intended victims that missionaries have rescued.

The Bagobos are very superstitious, and their customs are frequently very ridiculous. When one of them becomes possessed of an evil impulse (and the appearance of a snake in the house, the breaking of a pot on the fire, etc., is sufficient for this) he calls on his *Matanon* to liberate him from evil through his great knowledge. *Matanon*, the protector of the religion and customs of his forefathers, makes with his knife a doll in the form of a man; and then addressing God, says: "Oh God, creator of men, trees and all things, do not deprive us of life, but receive in place thereof this piece of wood which has our form." This ceremonial over, they throw a sack into the water which contains a little rice or "*morisqueta*"[4] (sometimes it contains the wooden doll also), and this is even accompanied occasionally by a cock. In this way the trouble is relieved. When they are sick they make offerings to the "*Diuata*" on their "*tambora*," which consists of a plate placed on top of a piece of bamboo set upright in the ground. On this plate are placed "*buyo*"[5] and tobacco, and then they address God, saying: "We offer you this, give us health." When they visit the sick they bind wires around their wrists and ankles to keep the "*limocod*" or soul from escaping. And when one dies he must have his ration of rice to eat on the way. Upon gathering the harvest of rice or corn, the very first grains obtained are offered to the "*Diuata*" and they would not think of selling or otherwise using any of the crop for themselves until their field implements have been fed, for these have cleaned the field.

The song, or cry, of the *limacon*[6] is for them the voice of God, and presages good or ill according to circumstances. Thus when the *limacon* cries out, all who hear it pause and look around. If, for example, they see a fallen tree, the *limacon* tells them that they should not continue their journey for they will meet the same fate as the trees; whereupon they turn back. Should they not behold anything that especially augurs ill, then the cry of the *limacon* has but assured them of the successful outcome of their journey, and they continue on their way. A sneeze is a bad augury, and when anyone sneezes at the beginning of a journey, the journey is postponed until the next day.

Few thefts are committed among Bagobos, for they believe that a thief can easily be discovered through their wonderful "*bongat*." This consists of two small joints of bamboo, containing mysterious powders. He from whom something has been stolen and who wishes to find the thief, takes a hen's egg, makes a hole in the shell and into this injects some of the mysterious powders already referred to and then places the egg in the fire. Should he desire the death of the thief, he has only to break the egg. But, as frequently happens, the thief may be a relative or a person very dear to the operator; and so oftentimes the egg is not broken in order that a more happy solution may be had; for in any case when all methods save breaking the egg have been resorted to, and the latter is done, no matter where the thief may be, he will at once betray himself by shouting "I am the thief, I am the thief!" And this is due to the sharp pains he is said to feel throughout his body. Once discovered, he can be cured by placing some of the powder from the other joint in water and bathing his body

[4] Cooked rice.

[5] Buyo is composed of the fruit of the betel-nut palm, locally known as *bonga* (*Areca catechu* Linn.), the fresh leaves of *Piper betle* Linn., and lime, to which tobacco is sometimes added. It is extensively chewed by the natives of India and Malaya.

[6] A small, brown pigeon, of the genus *Phapitroron*.

with it. This practice is very common among the pagans and Moros here. A converted Bagobo, named Anas, gave the writer a "*bongat*," the possession of which caused the former to be greatly feared while he was a pagan.

In a fourth letter, dated Davao, July 26, 1886, the following information is given:

The writer cites the case of one Maglandao (not a slave), who obtained a pair of earrings for which he could not pay; whereupon he agreed with the owner to work out the price, which was about 10 pesos. Some days later the owner of the earrings grew angry with him over some trivial matter and shot him, wounding him mortally. The offender was not a Bagobo, but hearing that the Bagobos were about to make a sacrifice, he sold them the dying man for fourteen cavans of rice. The purchasers were well pleased with the bargain, since they secured the victim cheap, as was also the other party to the transaction, for he had obtained sufficient rice to maintain himself for a year. The writer learned of this from a Bagobo who assisted at the sacrifice, and whom the writer baptized later. Both pagans and Moros make a business of selling victims to Bagobos. When a certain governor of the district of Davao expressed his disgust at this practice, a Bagobo replied: "Is it not lawful to spend your money as you wish? Our slaves are the same as money to us, and we dispose of them agreeably to our pleasure and customs." The writer holds them to be more barbarous than the Ammonites who sacrificed to Saturn; for these made sacrifices only at a certain period of the year, while the Bagobos make them continuously.[7] Every rancheria has its feasts in honor of the devil every year. He is known as *Busao, Mandaragan, Darago,* and by many other names. When a feast is to be held in his honor, there is a gathering in the house of the headman where all eat, drink, sing and dance very gaily; and the only objectionable feature of the occasion that one can see is the drunkenness commonly attendant on such occasions. They pass around their liquor, inviting one another to drink, and finally calling upon the master of the feast for a speech, they drink to the great *Darago,* promising to follow and honor him always, and like their forefathers, give him plenty of human blood to drink to secure his friendship and assistance in their wars. The inexperienced observer, who does not understand their language, sees nothing surprising in this; while he who knows something of the Bagobos will at once recognize the proof of the previous day's sacrifice namely the branches placed in the joint of bamboo before which the master of ceremonies invokes the *Darago,* for these tell the story.

When a contagious disease makes its appearance, or when a relative dies, they interpret this to mean that the *Darago* wants more victims, and immediately take steps to appease him and thereby save themselves from death. At the moment of sacrificing they say, "Aoaton mo ian dipanoc ini Manobo, timbac dipanoc co, so canac man sapi," which means "Receive thou the blood of this slave as if it were my blood, for I have bought it to offer it to thee." These words they pronounce while slashing the victim with their knives. As the great devil feeds continuously on human victims, these sacrifices must be numerous.

The following is taken from the *Historia de Mindanao y Jolo,* by P. Francisco Combes, S. J., pages 63 and 64:

The Bagobos, of a pure Indonesian race, are firmly planted on the smaller ridges of the southeast of Apo and have, therefore, as neighbors the Guiangas, the

[7] This is contradicted in Governor Walker's report. See p. 195.

Atas and the Calaganes. Moreover, they practice the barbarous customs of human sacrifices, are bold, warlike and given to drunkenness; almost all of them are of fine presence, for they immediately strangle deformed ones at birth. There are more than 12,000 of them, of whom in 1887 some 800 had been baptized:

Montano and Schadenberg, and the Jesuit Fathers Gisbert and Doyle, have made especial studies of the Bagobos. Since the year 1886 only one report of a sacrifice has been recorded. It is referred to, but with no details, by Sawyer. Every detail of the following story was thoroughly investigated and is vouched for by Governor Walker and Captain Plattka, senior Constabulary inspector of the district, and I have been furnished signed copies of their reports by General Bliss, governor of the Moro Province, with his permission to publish the facts. The event was the offering of a human sacrifice to the god of evil. The place was Talon and the date December 9, 1907. I give Governor Walker's report almost in its entirety, omitting only the names of the participants:

In addition to a pencil report made under date of December 20, 1907, regarding a human sacrifice made by the Bagobos at Talon near Digos on December 9, 1907, I have the honor to submit herewith a full report of an investigation held by myself and the senior inspector of Constabulary at Davao.

We left Davao on the morning of the 27th of December and arrived at Digos in the afternoon of the same day. An order was immediately sent to the Bagobos of Talon to come down to Digos to meet us.

On the morning of the 30th the entire population of Talon, men, women and children to the number of almost one hundred and fifty, arrived at Digos. They were informed that it was reported that a human sacrifice had been made at their town and that the authorities desired to know if it was so.

Datu ——— replied that it was true that a sacrifice had been held as stated and that both he and his people were ready to tell all about it, as to the best of their belief they had committed no crime but had only followed a religious custom practiced by themselves and their ancestors from time immemorial.

From the statement made by Datu ——— and his followers, it appears as follows:

That the Bagobos have several gods,[8] "*Bacalad*," god of the spirits; "*Aganmole Manobo*," god of good, and his wife, the goddess "*Diuata*," "*Mandarangan*,"[9] the god of evil (corresponding perhaps to our devil), and to whom sacrifice is made in order to appease his wrath, which is shown by misfortune, years of drought or evil befalling the tribe or its members; it is at times necessary to offer him human sacrifice so that he will allow the spirits of the deceased to rest. They say that in case a Bagobo of rank or influence dies and his widow is unable to secure another husband it is necessary for her to offer sacrifice to appease the spirit of her departed husband in order that she may secure another. In order that these sacrifices be not made too frequently it is customary for the old men of the town to gather once each year during the time when a certain constellation of seven stars, three at a right angle to the other four, are seen in the heavens to the east at 7 o'clock in the evening; this is said to occur once a year during

[8] The fact that the names of the Bagobo gods as here given differ from those in quotations given above may be due to a misunderstanding of the interpreter or it may be that Bagobos in different localities have different names for their gods.

[9] *Mandarangan* is believed by the Tagakaolos to live in the crater of Apo.

the first part of the month of December. This constellation of stars is called by the Bagobos "Balatic" and is the sign of the sacrifice; that is, if a sacrifice is to occur, it must take place during the period when the stars are in this position. The old men meet and decide if enough misfortune has overtaken the tribe or village during the period since the last sacrifice to render necessary another tribute to the god of evil. It is not necessary to offer a sacrifice for each evil, but when the misfortunes are considerable, a sacrifice is held to cover all.

In this case it appears that two widows went to the datu and requested that he arrange a sacrifice to appease the spirits of their departed husbands who were bothering them. The datu called a meeting of the old men; there were present, besides himself, three other Bagobos, and these four decided that as there had not been a sacrifice since the great drought (about three years before), and that since that time many evils had befallen them, it would be well to offer a sacrifice. These four men were sent out to find a slave for the sacrifice, the finder becoming the chief of ceremonies. A henchman of the datu purchased from a Bagobo a Bilan slave boy named Sacum, about 8 years old, who was deaf and cross-eyed, and who had other defects of vision making him of little or no value as a laborer. This boy was originally received as a slave from a Bilan as a wedding present, when the Bagobo married the Bilan's daughter about a year before.

The henchman of the datu agreed to pay five *agongs* for the boy and took him to the house of a friend where arrangements were made for the sacrifice by calling on all who, for any reason had need to appease the evil spirits, to come and take part. Three days after the slave was brought to this house, the people met at Talon near the Inolia River a short distance from the house, this being the regular place of sacrifice. Among those present were sixty prominent men and twenty-two women of the tribe. (The datu whose picture is shown on Pl. I was there.)

Being taken from the house, the boy Sacum was seated on the ground near the place of sacrifice. He was naked but no other preparation was made with regard to his person. Upon a platform or bench of bamboo about 2 feet high and a foot or two square was placed a small basket or receptacle made of the bark of the *bunga* tree, in which each person present and taking part in the sacrifice placed a piece of betel nut; over this the men placed their head handkerchiefs and over the handkerchiefs the women laid strips of the bark of the *palma* tree. Upon this the men laid their bolos, and spears were then stuck in the ground in a circle around the platform. Next, the datu, as chief of the sacrifice, made an oration which was about as follows:

"O Mandarangan, chief of evil spirits and all the other spirits, come to our feast and accept our sacrifice. Let this sacrifice appease your wrath and take from us our misfortunes, granting us better times."

After this the boy Sacum was brought forward, and placed against a small tree about 6 feet high; his hands were tied above his head and his body was tied to the tree with rattan strips at the waist and knees. A spear was then placed at his right side at a point below the right arm and above the margin of the rib. This lance was grasped by the two widows who, at a signal from the leader of the sacrifice, forced it through the child's body, so that it came out on the other side. The spear was then immediately withdrawn and the body cut in two at the waist by bolos in the hands of two Bagobo men, after which the body was cut down and chopped into bits by the people present, each of whom was allowed to take a small portion as a memento of the occasion, the remainder of the body being buried in a hole prepared for it.

It is said that the child was deaf and almost blind and that he did not realize

what was to happen to him until the moment he was tied, when he began to cry; and furthermore, that death was almost instantaneous, the only cry being one uttered when the spear first entered his side.

Datu ———, a man about 60 years of age, says that in his life he has attended or officiated at fifty human sacrifices, more or less, both among the Bagobos and Bilans, and that human sacrifice is also a practice among the Tagakaolos, although he has never been present at one held by that tribe. The Bagobos do not sacrifice any but old and decrepit or useless slaves captured from other tribes, but the Bilans sacrifice even their own people. Being asked if it was customary to eat any portion of the body sacrificed, my informant replied that it was not customary nor did he know of any case where such a thing had occurred.

The last sacrifice previous to this was held at Talon during the year of the drought (about 1905) when a Bilan slave, an old man who was paralyzed in one arm, was sacrificed by Datu ———, his master. When asked if the sacrifice of an animal would not do as well as that of a human being, they said no, better to have no sacrifice at all. They appeared utterly unconscious of having committed any crime, told their story with frankness, said it was a matter not talked about among their own people, but that if we wanted to know the facts they would give them to the authorities. They maintained that the offering of human sacrifices by their tribe was an old custom and as far as they knew was the only way to appease the wrath of the evil spirits, but they said if they were ordered to give the custom up they would do so even if the devil got them all.

In view of the facts in this case as brought out in the investigation, it is not thought that it is a case for prosecution before the courts, but rather one for religious instruction in so far as it is possible to give it. When it is considered that only a year and a half ago these people could not be approached by a white man without taking to the brush, and that now they will come down out of the mountains to meet the officials to discuss a question of this kind, it is evident that they have great confidence in our Government.

I explained to them that human sacrifices were wrong and would not be allowed by our Government, and furthermore that I could not let them off, but would write and explain everything to the provincial governor, who would decide what was to be done in the premises. These people have promised me that if I would assist them to secure a good location near the coast, they would move down from the mountains. I have promised them my assistance in the matter and I intend to try and get them down to a point near Digos in the near future.

These accounts differ in minor points, but the essential details agree very well. I know of no white man who has witnessed this event. The fact that none of our party learned about the sacrifice until we had passed through the place where it took place shows how secret the whole affair was kept. The native foreman on a near-by American plantation, where we stopped for a day or two, was the principal actor in the scene.

The Bagobos are, on the whole, very tractable and well disposed toward Americans, in spite of this primitive and bloody custom. I lived among them for several days and felt not the least anxiety. Good judgment and tact in dealing with them will doubtless enable the provincial officials to induce them to give up this practice even though they have made human sacrifices for many years.

WARREN D. SMITH.

PLATE I. TONGKALIN AND HIS HOUSEHOLD.

PLATE II. TONGKALING'S HOUSE ON THE EASTERN SLOPE OF MOUNT APO.

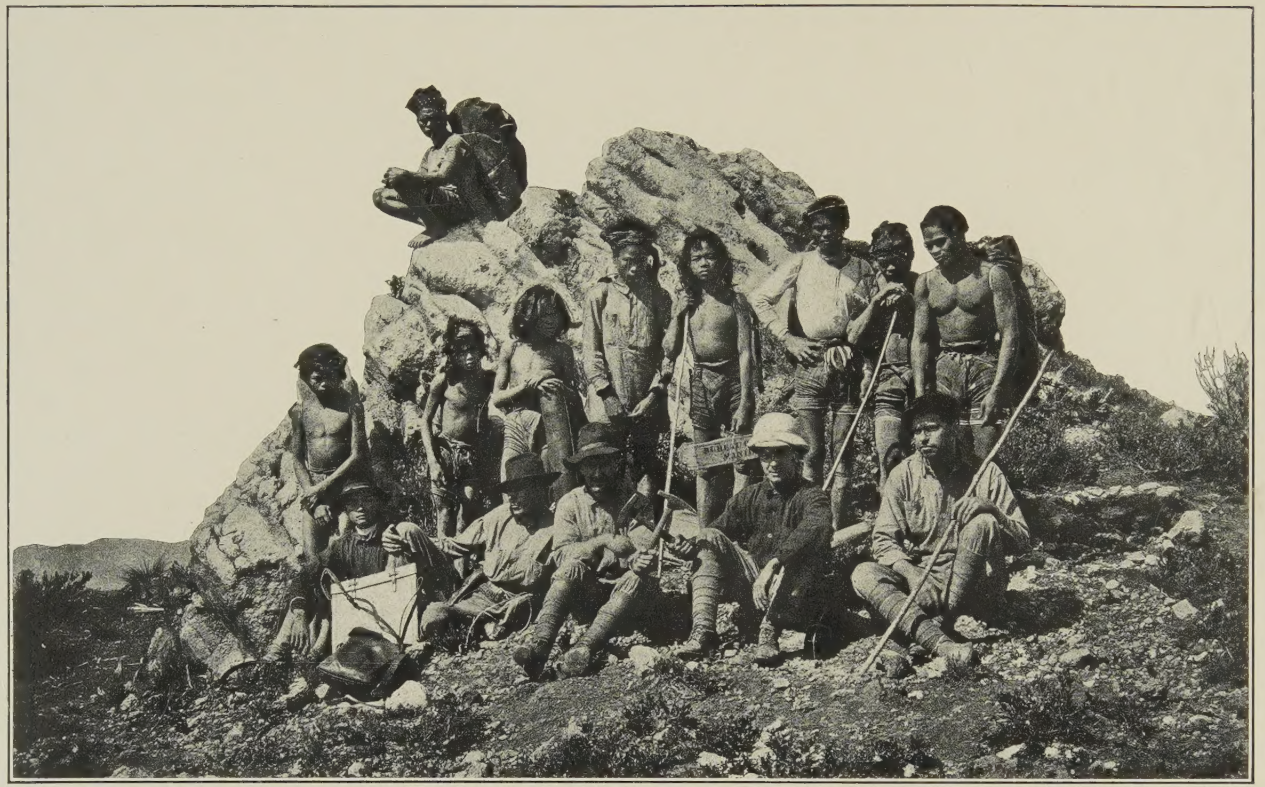


PLATE III. OUR PARTY ON THE SUMMIT OF MOUNT APO (THE PORTERS ARE BAGOBOS).